CONSUMER CHEMISTRY



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Consumer Chemistry

Anne Cline

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This text was compiled on 03/11/2026

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Licensing

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CHAPTER OVERVIEW

1: Introduction to Chemistry



Figure **1.1** (Public Domain; User:Phanton/Wikipedia via https://commons.wikimedia.org/wiki/F...tive_Soaps.jpg)

How does soap relate to chemistry?

Chemistry affects every area of our lives. Here is just one example of chemistry in action – the making of soaps. Soap was once made by boiling animal fat in ashes – the product was hard on the skin and not very pleasant to use. Today, soap manufacture involves complicated chemical processes to provide a wide variety of soaps for different skin types. Colors and odors can be custom-made for that individual experience.

"What is this made of? How can we produce this material quickly and at a low cost? Will this product harm us or help us?"—these are all questions that can be answered using the science of chemistry.

What is Chemistry?

Science is a general term used to describe the principled, rigorous study of the natural world. Many interconnected disciplines fall under this broader concept. For example, physics is the study of motion and forces. Biology is the study of living things. Geology is the study of the Earth and the rocks and minerals of which it is comprised. Chemistry is the study of the composition of matter and the changes that matter undergoes. Matter is anything that has mass and takes up space. Virtually everything around us is matter, including both living and nonliving things. Chemistry affects nearly everything we see and every action we take. Chemistry explains why milk that is left in the refrigerator for too long turns sour. Chemistry explains why certain pollutants called chlorofluorocarbons have done lasting damage to the ozone layer of our planet. Chemistry explains why the leaves of deciduous trees turn from green in the summer to various shades of red and yellow in the autumn (Figure below).



Figure **1.2**: Chemical reactions in the leaves of deciduous trees cause them to change color from green to red, orange, or yellow before dropping to the ground. (Public Domain; User:Jongleur100/Wikimedia Commons via https://commons.wikimedia.org/wiki/F...untry_lane.jpg)

Chemistry touches every area of our lives. The medicines we take, the food we eat, the clothes we wear—all of these materials and more are, in some way or another, products of chemistry.



Chemists look at the world in two ways, often simultaneously. The two worlds of the chemist are the **macroscopic** world and the **microscopic** world. Macroscopic refers to substances and objects that can be seen, touched, and measured directly. Microscopic refers to the small particles that make up all matter. Chemists must observe matter and do experiments macroscopically; then make generalizations and propose explanations that are microscopic in nature. For example, anyone can observe the physical change in appearance that occurs as an iron object, such as a tractor, is left out in the elements and gradually turns to rust. However, a chemist looking at the rusting tractor considers the individual atoms that make up the iron, and how they are changing as a result of exposure to oxygen in the air, and water from rain. Throughout the study of chemistry, there is often a switch back and forth between the macroscopic and microscopic worlds.



Figure **1.3**: Rusting artillery shells. (the US Marine Corps, Source: http://commons.wikimedia.org/wiki/File:USMC-060507-M-7799R-003.jpg; License: Public Domain)

Summary

- Chemistry is the study of matter and the changes it undergoes.
- Chemistry considers both macroscopic and microscopic information.

Review

1. Give two examples of chemistry in your everyday life.
2. What is the macroscopic world?
3. What is the microscopic world?

Explore More

1. Read the label on a prepared food product (for example: bread, cereal, dessert). List all of the ingredients in the product. Look up each ingredient on the Internet and write down what that material is doing in the food product.
2. Select your favorite hobby or activity. List all of the items you use in that activity or hobby. For each item, find out how chemistry has contributed to the creation or better operation of that item.

1.1: What Is This Made Of?

1.2: Prelude to Chemistry

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1.1: What Is This Made Of?

Welcome to Consumer Chemistry. What is this made of? How can we produce this material quicker and at lower cost? Will this produce harm us or help us? All of these questions can be answered using the science of **chemistry**.

What is Chemistry?

If we look up the word "chemistry" in the dictionary, we'll find something like this: "The science of the composition, structure, properties, and reactions of **matter**, especially of atomic and molecular systems" (Free Online Dictionary). This definition is certainly accurate, but does not give a good picture of the scope of chemistry or of the many interesting aspects of the field.

Chemistry touches every area of our lives. The medicines we take, the food we eat, the clothes we wear - all these materials and more are, in some way or another, products of chemistry.

What is the World Made Of?

Questions about matter have been asked for centuries. The ancient Greek philosophers spent a lot of time trying to figure out what matter was. Different philosophers debated whether matter was earth, water, air, fire, or some combination. They argued, but did not do any experiments at that time.

It took many centuries for humans to develop a better concept of what matter really is. Even today, we have an incomplete picture of exactly what this stuff is that we can touch and see. Chemistry involves the study of these substances, both in terms of basic properties and also learning all the things we can do with matter.

Chemists look at the world in two ways, often simultaneously. The two worlds of the chemist are the **macroscopic** world and the **microscopic** world. Macroscopic refers to substances and objects that can be seen, touched, and measured directly. Microscopic refers to the small particles that make up all matter. Chemists must observe matter and do experiments macroscopically and then make generalizations and propose explanations that are microscopic in nature. For example, anyone can observe the physical change in appearance that occurs as an iron object such as a tractor that is left out in the elements gradually turns to rust. However, a chemist looks at the rusting tractor and thinks about what is going on with the individual atoms that make up the iron and how they are changing as a result of exposure to oxygen in the air and water from rain. Throughout your study of chemistry, you will often switch back and forth between the macroscopic and microscopic worlds.



Figure **1.1.1**: *Rusting artillery shells.*

Summary

Chemistry is the study of matter and the changes it undergoes. Chemistry considers both macroscopic and microscopic information.

Explore More

1. Read the label on a prepared food product (for example: bread, cereal, dessert). List all the ingredients in the product. Look up each ingredient on the Internet and write down what that material is doing in the food product.
2. Select your favorite hobby or activity. List all the items you use in that activity or hobby. For each item, find out how chemistry has contributed to the creation or better operation of that item.

Contributors

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1.2: Prelude to Chemistry

If you are reading these words, you are likely starting a chemistry course. Get ready for a fantastic journey through a world of wonder, delight, and knowledge. One of the themes of this book is "chemistry is everywhere," and indeed it is; you would not be alive if it were not for chemistry, because your body is a big chemical machine.



Figure **1.2.1** © Thinkstock

6 images showing a volcanic eruption, large dinner spread, explosion, red wine, a pool of large fish, and molecules are laid out together.

If you do not believe it, do not worry. Every chapter in this book contains examples that will show you how chemistry is, in fact, everywhere. So enjoy the ride, and enjoy chemistry.

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1.3: What is Chemistry?

Learning Objectives

- To recognize the breadth, depth, and scope of chemistry.
- Define chemistry in relation to other sciences.
- Identify the main disciplines of chemistry.
- Match a scientific project with the correct type of chemist.

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

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure **1.3.1**). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

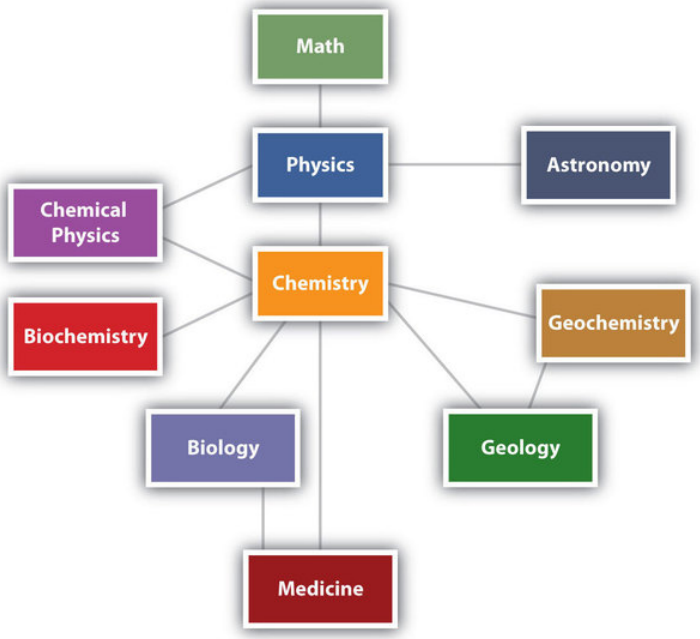


Figure **1.3.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

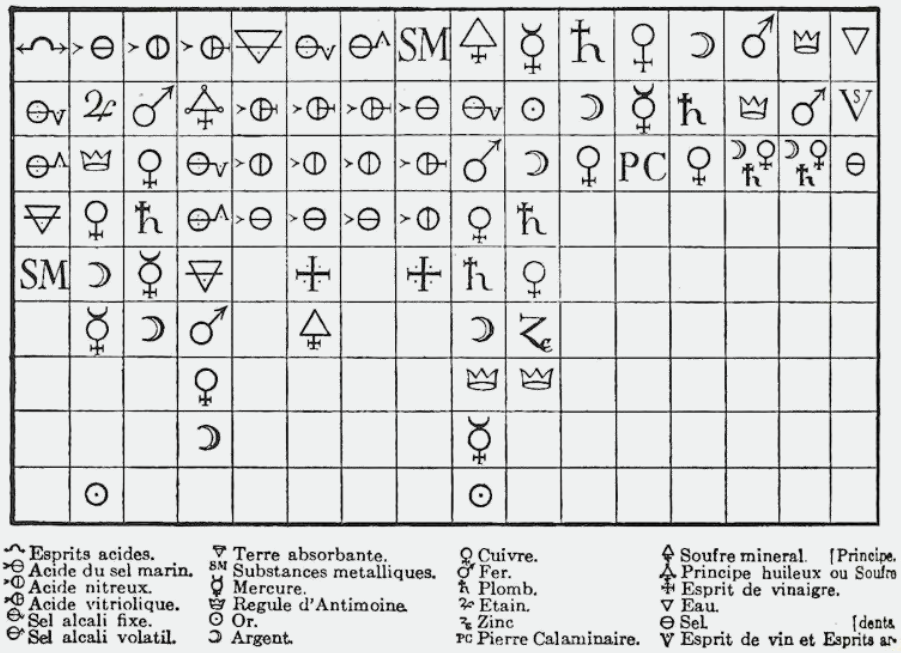
Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure **1.3.1** shows how many of the individual fields of science are related.

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

Alchemy Is in No way Chemistry!

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

Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Practitioners, called alchemists, thought that all matter was composed of different proportions of the four basic elements—fire, water, earth, and air—and believed that if you changed the relative proportions of these elements in a substance, you could change the substance. The long-standing attempts to “transmute” common metals into gold represented one goal of alchemy. Alchemy’s other major goal was to synthesize the philosopher’s stone, a material that could impart long life—even immortality. Alchemists used symbols to represent substances, some of which are shown in the accompanying figure. This was not done to better communicate ideas, as chemists do today, but to maintain the secrecy of alchemical knowledge, keeping others from sharing in it.



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

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

Alchemy and the ACS (American Chemical Society)

While watching the video below and answer the following questions.



Questions

1. What was the chief goal of an alchemist according to the video?

2. What could the philosopher's stone do to urine?
3. Is Alchemy a true science?
4. When urine is boiled down to a white paste, what is the name and symbol for the element that was obtained?
5. List some properties of this element that were discussed in the video.
6. Did wealthy people produce more of this element than poorer people?
7. What types of applications (applied science) did this element lead us to?
8. Instead of collecting urine, how can one collect higher concentrations of this element?
9. The video discussed phosphoric acid (formula: H_3PO_4). Name all the elements in this compound.
10. What were the mentioned applications of phosphoric acid?
11. What are some of the organic and biochemical applications of element 13?

Areas of Chemistry

The study of modern chemistry has many branches, but can generally be broken down into five main disciplines, or areas of study:

- **Physical chemistry:** Physical chemistry is the study of macroscopic properties, atomic properties, and phenomena in chemical systems. A physical chemist may study such things as the rates of chemical reactions, the energy transfers that occur in reactions, or the physical structure of materials at the molecular level.
- **Organic chemistry:** Organic chemistry is the study of chemicals containing carbon with hydrogen. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far). Most of the chemicals found in all living organisms are based on carbon.
- **Inorganic chemistry:** Inorganic chemistry is the study of chemicals that do not, in general, contain carbon. Inorganic chemicals are commonly found in rocks and minerals. One current important area of inorganic chemistry deals with the design and properties of materials involved in energy and information technology.
- **Analytical chemistry:** Analytical chemistry is the study of the composition of matter. It focuses on separating, identifying, and quantifying chemicals in samples of matter. An analytical chemist may use complex instruments to analyze an unknown material in order to determine its various components.
- **Biochemistry:** Biochemistry is the study of chemical processes that occur in living things. Research may cover basic cellular processes up to understanding disease states so better treatments can be developed.



Figure **1.3.2**: (left) Measurement of trace metals using atomic spectroscopy. (right) Measuring hormone concentrations.

In practice, chemical research is often not limited to just one of the five major disciplines. A particular chemist may use biochemistry to isolate a particular chemical found in the human body such as hemoglobin, the oxygen-carrying component of red blood cells. He or she may then proceed to analyze the hemoglobin using methods that would pertain to the areas of physical or analytical chemistry. Many chemists specialize in areas that are combinations of the main disciplines, such as bioorganic chemistry or physical organic chemistry.

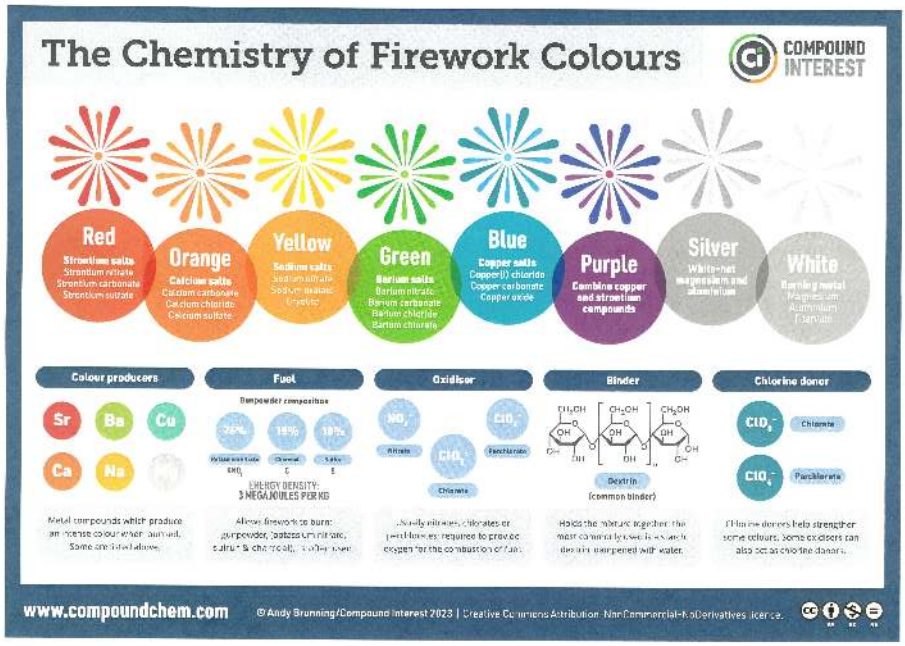


Figure **1.3.3**: The Chemistry of Firework Colours. (CC-BY-NC-ND; Andy Brunning)

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1.4: Basic Definitions

Learning Objective

- Learn the basic terms used to describe matter

The definition of chemistry—the study of the interactions of matter with other matter and with energy—uses some terms that should also be defined. We start the study of chemistry by defining basic terms.

Matter

Matter is anything that has mass and takes up space. A book is matter, a computer is matter, food is matter, and dirt in the ground is matter. Sometimes matter may be difficult to identify. For example, air is matter, but because it is so thin compared to other matter (e.g., a book, a computer, food, and dirt), we sometimes forget that air has mass and takes up space. Things that are not matter include thoughts, ideas, emotions, and hopes.

Example 1.4.1

Which of the following is matter and not matter?

a. a hot dog
b. love
c. a tree

Solution

a. A hot dog has mass and takes up space, so it is matter.
b. Love is an emotion, and emotions are not matter.
c. A tree has mass and takes up space, so it is matter.

Exercise 1.4.1

Which of the following is matter and not matter?

a. the moon
b. an idea for a new invention

Answer a

The moon is matter.

Answer b

The invention itself may be matter, but the idea for it is not.

To understand matter and how it changes, we need to be able to describe matter. There are two basic ways to describe matter: physical properties and chemical properties.

Physical properties

Physical properties are characteristics that describe matter as it exists. Some physical characteristics of matter are shape, color, size, and temperature. An important physical property is the **phase** (or **state**) of matter. The three fundamental phases of matter are solid, liquid, and gas (Figure **1.4.1**).



Figure 1.4.1: The Phases of Matter. Chemistry recognizes three fundamental phases of matter: solid (left), liquid (middle), and gas (right). (CC BY-SA 3.0; Spirit469). The solid state depicted is an ice sculpture of an angel, the liquid state is a drop of water, and the gas is clouds made of water vapor.

Chemical Properties

Chemical properties are characteristics of matter that describe how matter changes form in the presence of other matter. Does a sample of matter burn? Burning is a chemical property. Does it behave violently when put in water? This reaction is a chemical property as well (Figure 1.4.2). In the following chapters, we will see how descriptions of physical and chemical properties are important aspects of chemistry.



Figure 1.4.2: Chemical Properties. The fact that this match burns is a chemical property of the match. (Sebastian Ritter (Rise0011)).

Physical Change

A physical change occurs when a sample of matter changes one or more of its physical properties. For example, a solid may melt (Figure 1.4.3), or alcohol in a thermometer may change volume as the temperature changes. A physical change does not affect the chemical composition of matter.



Figure 1.4.2: Physical Changes: The solid ice melts into liquid water—a physical change. A time-lapse animation of ice cubes melting in a glass over 50 minutes. (Public Domain; Moussa).

Chemical Change

Chemical change is the process of demonstrating a chemical property, such as the burning match in Figure 1.4.2 "Chemical Properties". As the matter in the match burns, its chemical composition changes, and new forms of matter with new physical properties are created. Note that chemical changes are frequently accompanied by physical changes, as the new matter will likely have different physical properties from the original matter.

Example 1.4.2

Describe each process as a physical change or a chemical change.

a. Water in the air turns into snow.
b. A person's hair is cut.
c. Bread dough becomes fresh bread in an oven.

Solution

a. Because the water is going from a gas phase to a solid phase, this is a physical change.
b. Your long hair is being shortened. This is a physical change.
c. Because of the oven's temperature, chemical changes are occurring in the bread dough to make fresh bread. These are chemical changes. (In fact, a lot of cooking involves chemical changes.)

Exercise 1.4.2

Identify each process as a physical change or a chemical change.

a. A fire is raging in a fireplace.
b. Water is warmed to make a cup of coffee.

Answer a

chemical change

Answer b

physical change

Substance

A sample of matter that has the same physical and chemical properties throughout is called a substance. Sometimes the phrase *pure substance* is used, but the word *pure* isn't needed. The definition of the term *substance* is an example of how chemistry has a specific definition for a word that is used in everyday language with a different, vaguer definition. Here, we will use the term *substance* with its strict chemical definition.

> *Chemistry recognizes two different types of substances: elements and compounds.*

Element

An element is the simplest type of chemical substance; it cannot be broken down into simpler chemical substances by ordinary chemical means. There are 118 elements known to science, of which 80 are stable. (The other elements are radioactive, a condition we will consider in Chapter 15.) Each element has its own unique set of physical and chemical properties. Examples of elements include iron, carbon, and gold.

Compound

A compound is a combination of more than one element. The physical and chemical properties of a compound are different from the physical and chemical properties of its constituent elements; that is, it behaves as a completely different substance. There are over 50 million compounds known, and more are being discovered daily. Examples of compounds include water, penicillin, and sodium chloride (the chemical name for common table salt).

Mixtures

Physical combinations of more than one substance are called mixtures. Elements and compounds are not the only ways in which matter can be present. We frequently encounter objects that are physical combinations of more than one element or compound—mixtures. There are two types of mixtures.

Heterogeneous Mixture

A heterogeneous mixture is a mixture composed of two or more substances. It is easy to tell, sometimes by the naked eye, that more than one substance is present.

Homogeneous Mixture/ Solution

A homogeneous mixture is a combination of two or more substances that is so intimately mixed, that the mixture behaves as a single substance. Another word for a homogeneous mixture is a solution. Thus, a combination of salt and steel wool is a heterogeneous mixture because it is easy to see which particles of the matter are salt crystals and which are steel wool. On the other hand, if you take salt crystals and dissolve them in water, it is very difficult to tell that you have more than one substance present just by looking—even if you use a powerful microscope. The salt dissolved in water is a homogeneous mixture, or a solution (Figure **1.4.3**).



Figure **1.4.3**: Types of Mixtures © Thinkstock. On the left, the combination of two substances is a heterogeneous mixture because the particles of the two components look different. On the right, the salt crystals have dissolved in the water so finely that you cannot tell that salt is present. The homogeneous mixture appears like a single substance.

✔ Example 1.4.3

Identify the following combinations as heterogeneous mixtures or homogenous mixtures.

a. soda water (carbon dioxide is dissolved in water)
b. a mixture of iron metal filings and sulfur powder (both iron and sulfur are elements)

Solution

a. Because carbon dioxide is dissolved in water, we can infer from the behavior of salt crystals dissolved in water that carbon dioxide dissolved in water is (also) a homogeneous mixture.
b. Assuming that the iron and sulfur are simply mixed together, it should be easy to see what is iron and what is sulfur, so this is a heterogeneous mixture.

? Exercise 1.4.3

a. the human body
b. an amalgam, a combination of some other metals dissolved in a small amount of mercury

Answer a

heterogeneous mixture

Answer b

homogeneous mixture

There are other descriptors that we can use to describe matter, especially elements. We can usually divide elements into metals and nonmetals, and each set shares certain (but not always all) properties.

Metal

A metal is an element that conducts electricity and heat well and is shiny, silvery, solid, ductile, and malleable. At room temperature, metals are solid (although mercury is a well-known exception). A metal is ductile because it can be drawn into thin wires (a property called *ductility*); and malleable because it can be pounded into thin sheets (a property called *malleability*).

Nonmetal

A non-metal is an element that is brittle when solid, and does not conduct electricity or heat very well. Non-metals cannot be made into thin sheets or wires (Figure **1.4.4**). Nonmetals also exist in a variety of phases and colors at room temperature.

Semi-metals

Some elements have properties of both metals and nonmetals and are called semi-metals (or metalloids). We will see later how these descriptions can be assigned rather easily to various elements.



Figure **1.4.4**: Semimetals © Thinkstock. On the left is some elemental mercury, the only metal that exists as a liquid at room temperature. It has all the other expected properties of a metal. On the right, elemental sulfur is a yellow nonmetal that usually is found as a powder.

Describing Matter Flowchart

"Describing Matter" is a flowchart of the relationships among the different ways of describing matter.

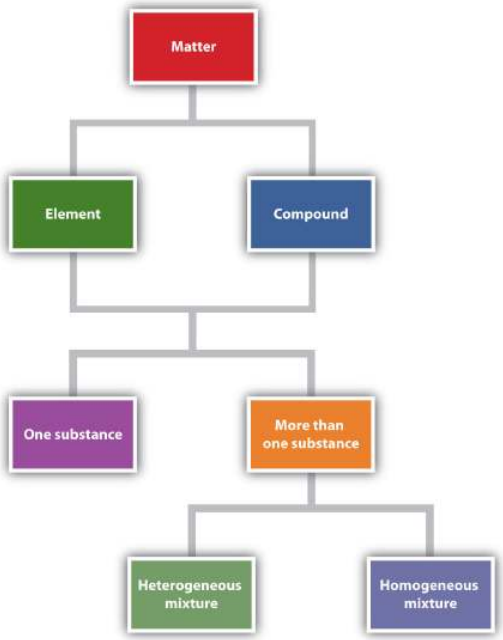


Figure 1.4.5: Describing Matter. This flowchart shows how matter can be described. Matter forks into element & compound which fork into 1 substance & more than 1 substance. More than 1 substance is homogenous or heterogenous.

Example 1.4.1: Chemistry is Everywhere: In the Morning

Most people have a morning ritual, a process that they go through every morning to get ready for the day. Chemistry appears in many of these activities.

- If you take a shower or bath in the morning, you probably use soap, shampoo, or both. These items contain chemicals that interact with the oil and dirt on your body and hair to remove them and wash them away. Many of these products also contain chemicals that make you smell good; they are called *fragrances*.
- When you brush your teeth in the morning, you usually use toothpaste, a form of soap, to clean your teeth. Toothpastes typically contain tiny, hard particles called *abrasives* that physically scrub your teeth. Many toothpastes also contain fluoride, a substance that chemically interacts with the surface of the teeth to help prevent cavities.
- Perhaps you take vitamins, supplements, or medicines every morning. Vitamins and other supplements contain chemicals your body needs in small amounts to function properly. Medicines are chemicals that help combat diseases and promote health.
- Perhaps you make some fried eggs for breakfast. Frying eggs involves heating them enough so that a chemical reaction occurs to cook the eggs.
- After you eat, the food in your stomach is chemically reacted so that the body (mostly the intestines) can absorb food, water, and other nutrients.
- If you drive or take the bus to school or work, you are using a vehicle that probably burns gasoline, a material that burns fairly easily and provides energy to power the vehicle. Recall that burning is a chemical change.

These are just a few examples of how chemistry impacts your everyday life. And we haven't even made it to lunch yet!



Figure 1.4.6: Chemistry in Real Life © Thinkstock. Examples of chemistry can be found everywhere—in personal hygiene products, food, and motor vehicles. Personal hygiene products (left), food (middle), and motor vehicles (right) images next to one another.

Key Takeaways

- Chemistry is the study of matter and its interactions with other matter and energy.
- Matter is anything that has mass and takes up space.
- Matter can be described in terms of physical properties and chemical properties.
- Physical properties and chemical properties of matter can change.
- Matter is composed of elements and compounds.
- Combinations of different substances are called mixtures.
- Elements can be described as metals, nonmetals, and semi-metals.

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1.4.1: Classification and Properties of Matter

Learning Objectives

- Use physical and chemical properties, including phase, to describe matter.
- Distinguish between physical and chemical changes.
- Identify a sample of matter as an element, a compound, or a mixture (homogeneous/heterogeneous).
- Distinguish between organic and inorganic chemicals.
- Label all atoms within an organic or inorganic compound.
- Recognize physical methods used to separate mixtures.

Physical and Chemical Properties

The properties that chemists use to describe matter fall into two general categories. Physical properties are characteristics that **describe** matter. They include characteristics such as size, shape, color, and mass. Many of these properties can be quantitative in nature. For example, quantitative physical properties of water would be the boiling point (100 °C / 212 °F), melting point (0°C / 32 °F) and density (1.00 g/ml at 4.0°C.

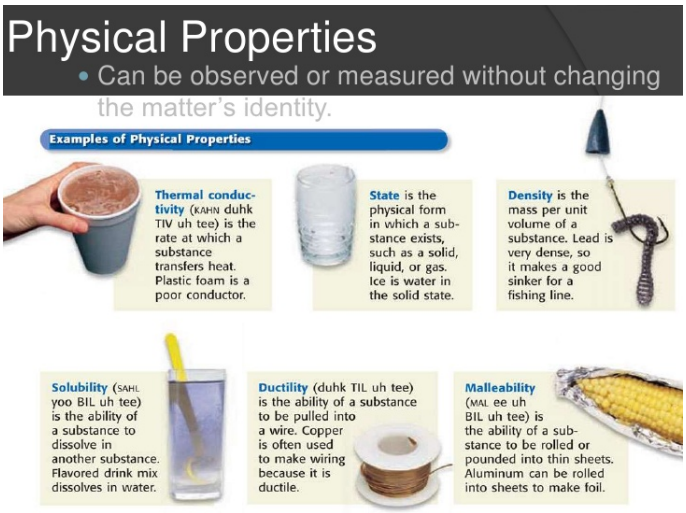


Figure **1.4.1.1**: Physical Properties. (Copyright;https://www.slideshare.net/cfoltz/ph...cal-properties)

Chemical properties are characteristics that describe how matter **changes** its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. Oxidation, rusting, decomposition, and inertness (not reactive) are chemical properties as well. Click on this video and record the physical and chemical properties of the element sodium.

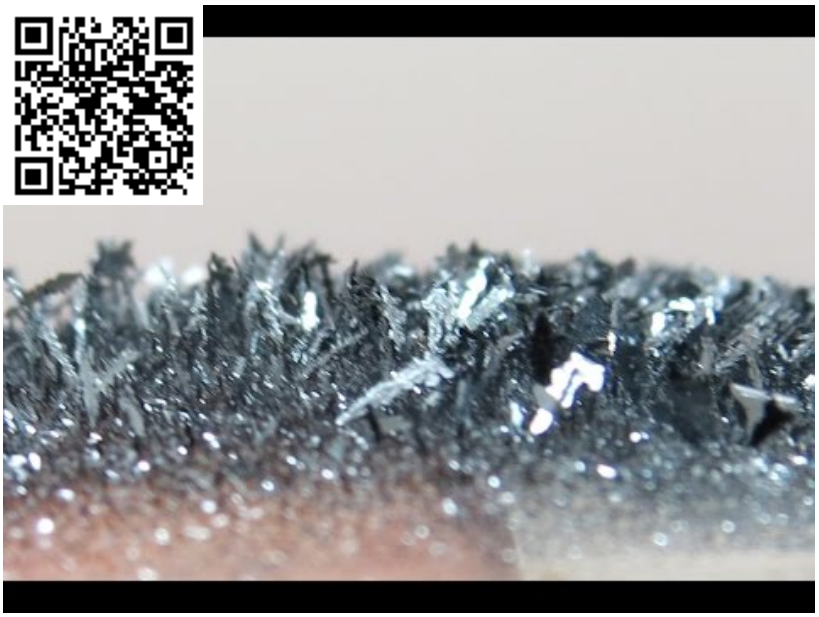


Figure **1.4.1.2**: Port Royal, South Carolina oxidation of iron. Image courtesy of Elizabeth R. Gordon.

States of Matter (phases)

Another way to classify matter is to describe it as a solid, a liquid, or a gas, which was done in the examples of solutions. These three descriptions, each implying that the matter has certain physical properties, represent the three phases of matter. A solid has a

definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers. We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas).



Video**1.4.1.1**: Sublimation and deposition of Iodine.

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a phase change, a physical process in which a substance goes from one phase to another (Figure **1.4.1.3**). Phase changes have particular names depending on what phases are involved, as summarized in Table **1.4.1.1**.

Table **1.4.1.1**: Phase Changes

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

Classification of Matter

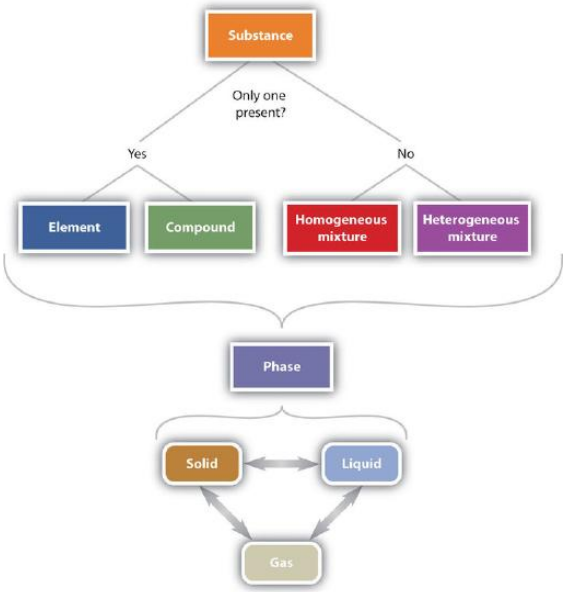


Figure **1.4.1.3**: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties. (Cc BY-NC-SA; anonymous)

Elements and Compounds

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

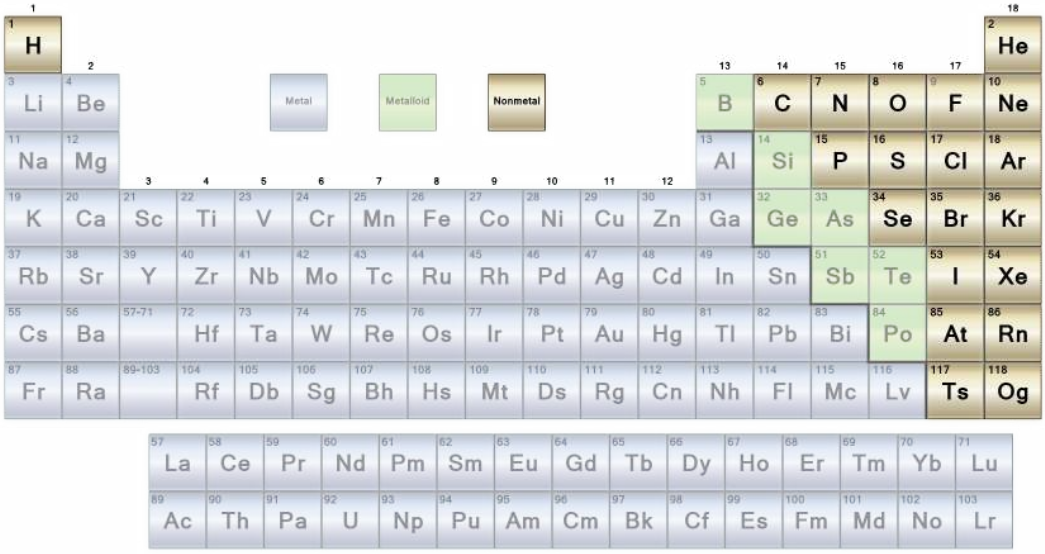


Figure **1.4.1.4**: Periodic-Table-Metals.jpg. (CC-BY-SA-4.0), https://commons.wikimedia.org/w/inde...edit&redlink=1.

Sometimes the word *pure* is added to a substance, but this is not absolutely necessary. By definition, any single substance is pure.

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

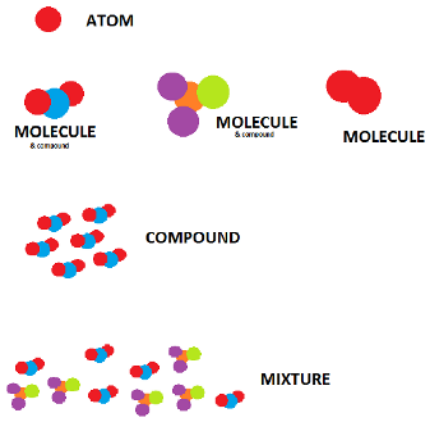


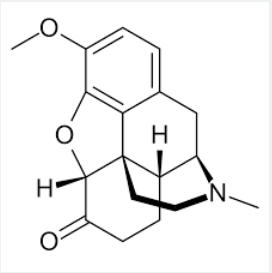
Figure **1.4.1.5**: Appreciating elements, molecules and compounds.

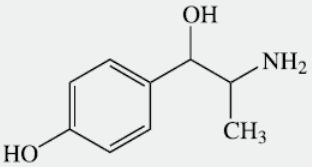
Inorganic and Organic Compounds

Compounds can be further classified as being inorganic or organic. Organic compounds contain carbon, hydrogen, and usually another element from the right side of the periodic table. Be careful when thinking about organic chemicals. In the real world, the term "organic" is typically used to describe products that have natural ingredients. In the world of science, the word "organic" is used to denote compounds that have carbon and hydrogen connections. Look at some of the structures below to get an appreciation of organic chemical structures.

Organic structures

The two molecules shown below are heavily used in the pharmaceutical industry. The compound on the left is known as hydrocodone. This is an opioid painkiller that is extremely addictive. It is regularly dispensed for surgical and chronic pain. The compound on the right is Adderall. This medication is used to treat ADHD and narcolepsy. Both of these medications are controlled by the DEA (Drug Enforcement Agency) and are illegal to possess unless you have a valid prescription.





Mixtures

A material composed of two or more substances is a mixture. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called **heterogeneous mixtures**. In some mixtures, the components are so intimately combined that they act like a single

substance (even though they are not). Mixtures with a consistent composition throughout are called **homogeneous mixtures** (or **solutions**). Sugar dissolved in water is an example of a solution. A metal alloy, such as steel, is an example of a solid solution. Air, a mixture of mainly nitrogen and oxygen, is a gaseous solution.

✔ Exercise 1.4.1.1

How would a scientist categorize each type 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 1.4.1.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a

Coffee could be a heterogeneous or homogeneous mixture. If insoluble parts are able to be identified, then it would be classified as being heterogeneous. If not, then coffee would be a homogeneous mixture or a solution.

Answer b

Hydrogen is an element. It can be located on the periodic table.

Answer c

An egg (assume raw) would be a heterogeneous mixture. The yolk and egg white are two different substances that can be easily seen.

? Exercise 1.4.1.3

a. Classify each as being element, compound, heterogeneous mixture, or homogeneous mixture (solution): air at Furman University, Furman Lake water, copper wire, and Furman tap water.
b. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
c. Which is/are physical change(s): burning of fuel, digestion of food, salt dissolving in water, copper conducting electricity, and water boiling.

Answer a

Hopefully, Furman air is a homogenous mixture (solution). If there is no burning or dust build-up in the area, this is safe to assume. Furman Lake is definitely a heterogeneous mixture (in some areas it can get a bit swampy). Copper wire is an element. There are very few elements in nature. Lastly, Furman tap water is usually a homogeneous mixture. Natural and

man-made chemicals are in our tap water (trust me, you want the chlorine). Our toilets do use greywater which can look heterogeneous (ok for sewer but not to drink).

Answer b

A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.

Answer c

The physical changes are salt dissolving water, copper conducting, and water boiling. If composition is not changed, then this is a physical change. If there is a method to physically separate the components (like boiling, evaporation, distillation, magnetism, or filtration), then a physical change has occurred.

Contributors and Attributions

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1.5: Chemistry as a Science

Learning Objective

- Learn what science is and how it works.

Chemistry is a branch of science. Although science itself is difficult to define exactly, the following definition can serve as a starting point. Science is the process of knowing about the natural universe through observation and experiment. Science is not the only process of knowing (e.g., the ancient Greeks simply sat and *thought*), but it has evolved over more than 350 years into the best process that humanity has devised, to date, to learn about the universe around us.

The process of science is usually stated as the *scientific method*, which is rather naively described as follows:

1. state a hypothesis,
2. test the hypothesis, and
3. refine the hypothesis

In actuality, the process is not that simple. (For example, a scientist does not go into their lab every day and exclaim, "I am going to state a hypothesis today and spend the day testing it!") The process is not that simple because science and scientists have a body of knowledge that has already been identified as coming from the highest level of understanding, and most scientists build from that body of knowledge.

An educated guess about how the natural universe works is called a **hypothesis**. A scientist who is familiar with how part of the natural universe works—say, a chemist—is interested in furthering that knowledge. That person makes a reasonable guess—a hypothesis—that is designed to see if the universe works in a new way as well. Here's an example of a hypothesis: "if I mix one part of hydrogen with one part of oxygen, I can make a substance that contains both elements."

> *For a hypothesis to be termed a scientific hypothesis, it has to be something that can be supported or refuted through carefully crafted experimentation or observation.*

Most good hypotheses are grounded in previously understood knowledge and represent a testable extension of that knowledge. The scientist then devises ways to test if that hypothesis is correct or not. That is, the scientist plans experiments. **Experiments are tests of the natural universe to see if a guess (hypothesis) is correct**. An experiment to test our previous hypothesis would be to actually mix hydrogen and oxygen and see what happens. Most experiments include observations of small, well-defined parts of the natural universe designed to see results of the experiments.

A Scientific Hypothesis

A hypothesis is often written in the form of an if/then statement that gives a possibility (if) and explains what may happen because of the possibility (then). For example, if eating elemental sulfur repels ticks, then someone that is eating sulfur every day will not get ticks.



Why do we have to do experiments? Why do we have to test? Because the natural universe is not always so obvious, experiments are necessary. For example, it is fairly obvious that if you drop an object from a height, it will fall. Several hundred years ago (coincidentally, near the inception of modern science), the concept of gravity explained that test. However, is it obvious that the

entire natural universe is composed of only about 115 fundamental chemical building blocks called elements? This wouldn't seem true if you looked at the world around you and saw all the different forms matter can take. In fact, the concept of *the element* is only about 200 years old, and the last naturally occurring element was identified about 80 years ago. It took decades of tests and millions of experiments to establish what the elements actually are. These are just two examples; a myriad of such examples exists in chemistry and science in general.

When enough evidence has been collected to establish a general principle of how the natural universe works, the evidence is summarized in a theory. A theory is a general statement that explains a large number of observations. "All matter is composed of atoms" is a general statement, a theory, that explains many observations in chemistry. A theory is a very powerful statement in science. There are many statements referred to as "the theory of _____" or the "_____ theory" in science (where the blanks represent a word or concept). When written in this way, theories indicate that science has an overwhelming amount of evidence of its correctness. We will see several theories in the course of this text.

A specific statement that is thought to never be violated by the entire natural universe is called a law. A scientific law is the highest understanding of the natural universe that science has and is thought to be inviolate. The fact that all matter attracts all other matter—the law of gravitation—is one such law. Note that the terms *theory* and *law* used in science have slightly different meanings from those in common usage; where theory is often used to mean hypothesis ("I have a theory…"), and a law is an arbitrary limitation that can be broken but with potential consequences (such as speed limits). Here again, science uses these terms differently, and it is important to apply their proper definitions when you use these words in science. (Figure 1.5.1)

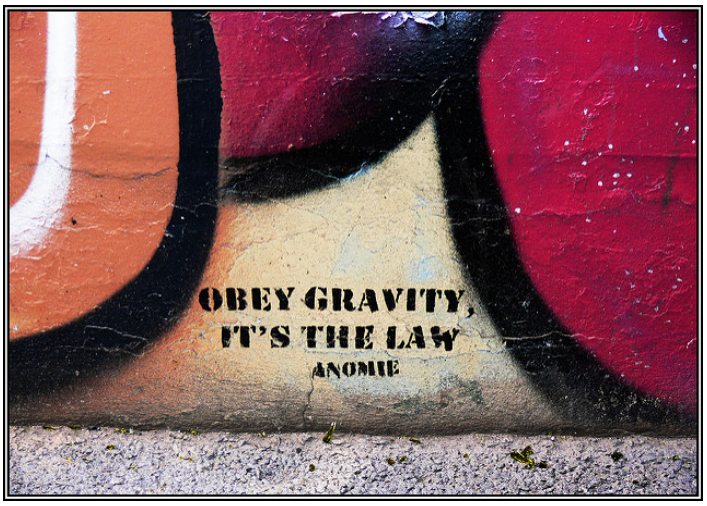


Figure 1.5.1: Defining a law. Does this graffiti mean "law" the way science defines "law"? (CC BY-SA-NC-ND; Koppenbadger).

There is an additional phrase in our definition of science: "the natural universe." Science is concerned *only* with the natural universe. What is the natural universe? It's anything that occurs around us, well, naturally. Stars, planets, the appearance of life on earth; as well as how animals, plants, and other matter function are all part of the natural universe. Science is concerned with that—and *only* that.

Of course, there are other things that concern us. For example, is the English language part of science? Most of us can easily answer no; English is not science. English is certainly worth knowing (at least for people in predominantly English-speaking countries), but why isn't it science? English, or any human language, is not science because ultimately it is *contrived*; it is made up. Think of it: the word spelled b-l-u-e represents a certain color, and we all agree what color that is. But what if we used the word h-a-r-d to describe that color? (Figure 1.5.2) That would be fine—as long as everyone agreed. Anyone who has learned a second language must initially wonder why a certain word is used to describe a certain concept; ultimately, the speakers of that language agreed that a particular word would represent a particular concept. It was contrived.

That doesn't mean language isn't worth knowing. It is very important in society. But it's not *science*. Science deals only with what occurs naturally.

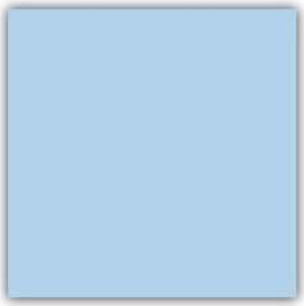


Figure 1.5.2: English Is Not Science. How would you describe this color? Blue or hard? Either way, you're not doing science.

Example 1.5.1: Identifying Science

Which of the following fields would be considered science?

a. geology, the study of the earth
b. ethics, the study of morality
c. political science, the study of governance
d. biology, the study of living organisms

Solution

a. Because the earth is a natural object, the study of it is indeed considered part of science.
b. Ethics is a branch of philosophy that deals with right and wrong. Although these are useful concepts, they are not science.
c. There are many forms of government, but all are created by humans. Despite the fact that the word *science* appears in its name, political science is not true science.
d. Living organisms are part of the natural universe, so the study of them is part of science.

Exercise 1.5.1

Which is part of science, and which is not?

a. dynamics, the study of systems that change over time
b. aesthetics, the concept of beauty

Answer A

science

Answer B

not science

The field of science has gotten so big that it is common to separate it into more specific fields. First, there is mathematics, the language of science. All scientific fields use mathematics to express themselves—some more than others. Physics and astronomy are scientific fields concerned with the fundamental interactions between matter and energy. Chemistry, as defined previously, is the study of the interactions of matter with other matter and with energy. Biology is the study of living organisms, while geology is the study of the earth. Other sciences can be named as well. Understand that these fields are not always completely separate; the boundaries between scientific fields are not always readily apparent. A scientist may be labeled a biochemist if he or she studies the chemistry of biological organisms.

Finally, understand that science can be either qualitative or quantitative. Qualitative implies a description of the quality of an object. For example, physical properties are generally qualitative descriptions: sulfur is yellow, your math book is heavy, or that statue is pretty. A quantitative description represents the specific amount of something; it means knowing how much of something is present, usually by counting or measuring it. Some quantitative descriptions include: 25 students in a class, 650 pages in a book, or a velocity of 66 miles per hour. Quantitative expressions are very important in science; they are also very important in chemistry.

Example 1.5.2: qualitative vs. quantitative Descriptions

Identify each statement as either a qualitative description or a quantitative description.

a. Gold metal is yellow.
b. A ream of paper has 500 sheets in it.
c. The weather outside is snowy.
d. The temperature outside is 24 degrees Fahrenheit.

Solution

a. Because we are describing a physical property of gold, this statement is qualitative.
b. This statement mentions a specific amount, so it is quantitative.
c. The word *snowy* is a description of how the day is; therefore, it is a qualitative statement.
d. In this case, the weather is described with a specific quantity—the temperature. Therefore, it is quantitative.

Exercise 1.5.2

Are these qualitative or quantitative statements?

a. Roses are red, and violets are blue.
b. Four score and seven years ago….

Answer A

qualitative

Answer B

quantitative

Food and Drink Application: Carbonated Beverages

Some of the simple chemical principles discussed in this chapter can be illustrated with carbonated beverages: sodas, beer, and sparkling wines. Each product is produced in a different way, but they all have one thing in common: they are solutions of carbon dioxide dissolved in water.

Carbon dioxide is a compound composed of carbon and oxygen. Under normal conditions, it is a gas. If you cool it down enough, it becomes a solid known as dry ice. Carbon dioxide is an important compound in the cycle of life on earth.

Even though it is a gas, carbon dioxide can dissolve in water, just like sugar or salt can dissolve in water. When that occurs, we have a homogeneous mixture, or a solution, of carbon dioxide in water. However, very little carbon dioxide can dissolve in water. If the atmosphere were pure carbon dioxide, the solution would be only about 0.07% carbon dioxide. In reality, the air is only about 0.03% carbon dioxide, so the amount of carbon dioxide in water is reduced proportionally.

However, when soda and beer are made, manufacturers do two important things: they use pure carbon dioxide gas, and they use it at very high pressures. With higher pressures, more carbon dioxide can dissolve in the water. When the soda or beer container is sealed, the high pressure of carbon dioxide gas remains inside the package. (Of course, there are more ingredients in soda and beer besides carbon dioxide and water.)

When you open a container of soda or beer, you hear a distinctive *hiss* as the excess carbon dioxide gas escapes. But something else happens as well. The carbon dioxide in the solution comes out of solution as a bunch of tiny bubbles. These bubbles impart a pleasing sensation in the mouth, so much so that the soda industry sold over *225 billion* servings of soda in the United States alone in 2009.

Some sparkling wines are made in the same way—by forcing carbon dioxide into regular wine. Some sparkling wines (including champagne) are made by sealing a bottle of wine with some yeast in it. The yeast *ferments*, a process by which the yeast converts sugars into energy and excess carbon dioxide. The carbon dioxide produced by the yeast dissolves in the wine.

Then, when the champagne bottle is opened, the increased pressure of carbon dioxide is released, and the drink bubbles just like an expensive glass of soda.



Figure **1.5.3**: Carbonated Beverages © Thinkstock. Soda, beer, and sparkling wine take advantage of the properties of a solution of carbon dioxide in water.

Soda (left), beer (middle) and sparkling wine (right) images next to one another.

Key Takeaways

- Science is a process of knowing about the natural universe through observation and experiment.
- Scientists go through a rigorous process to determine new knowledge about the universe; this process is generally referred to as the scientific method.
- Science is broken down into various fields, of which chemistry is one.
- Science, including chemistry, is both qualitative and quantitative.

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1.6: The Scientific Method

The Scientific Method is simply a framework for the systematic exploration of patterns in our world. It just so happens that this framework is extremely useful for the examination of chemistry and its many questions. The scientific process, an iterative process, uses the repeated acquisition and testing of data through experimental procedures to disprove hypotheses. A hypothesis is a proposed explanation of natural phenomena, and after a hypothesis has survived many rounds of testing, it may be accepted as a theory and used to explain the phenomena in question. Thus, the scientific method is not a linear process of steps, but a method of inductive reasoning.

Contributors and Attributions

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1.6.1: Limitations of the Scientific Method

Learning Objectives

- To understand the limitations in the scientific method, one must become familiar with the scientific method and its components.

Pseudo-science, basically "fake"-science," consists of scientific claims which are made to appear factual when they are actually false. Many people question whether Pseudo-science should even contain the word "science" as Pseudo-science isn't really even an imitation of science; it pretty much disregards the scientific method all together. Also known as alternative or fringe-science, Pseudo-science relies on invalid arguments called sophisms, a word Webster dictionary defines as "an argument apparently correct in form but actually invalid; especially : such an argument used to deceive". Pseudo-science usually lacks supporting evidence and does not abide by the scientific method. That is, pseudo-theories fail to use carefully cultivated and controlled experiments to test a hypothesis. A scientific hypothesis must include observable, empirical and testable data, and must allow other experts to test the hypothesis. Pseudo-science does not accomplish these goals. Several examples of Pseudo-Science include phrenology, astrology, homeopathy, reflexology and iridology.

Distinguishing Pseudo-Science

In order to distinguish a pseudoscience, one must look at the definition of science, and the aspects that make science what it is. Science is a process based on observations, conjectures, and assessments to provide better understanding of the natural phenomena of the world. Science generally always follows a formal system of inquiry which consists of observations, explanations, experiments, and lastly, hypothesis and predictions. Scientific theories are always challenged by experts and revised to fit new theories. Pseudo-science, however, is mostly based on beliefs and it greatly opposes contradictions. Their hypothesis are never revised to fit new data or information. Scientist continually disprove ideas to achieve a better understanding of the physical world, whereas pseudo-scienctists focus on proving theories to make their claims seem plausible. For example, science text books come out with new editions every couple of years to correct typos, update information, add new illustrations, etc. However, it has been observed that pseudo-science textbooks only come out with one edition, and is never updated or revised even if their theory has been proven to be false.

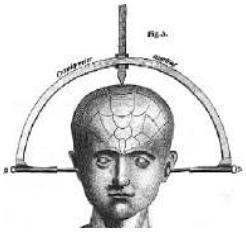
Pseudo-science beliefs often tend to be greatly exaggerated and very vague. Complicated technical language is often used to sound impressive but it is usually meaningless. For example, a phrase like "energy vibrations" is used to sound remarkable but a phrase like this is insignificant and doesn't really explain anything. Furthermore, Pseudo-science often consists of outrageous, yet unprovable claims. Thus, pseudo-scientists tend to focus on confirming their ideas, rather than finding evidence that refutes them. The following dialogue contains the thought-processes behind Pseudo-Science.

1. My friend and I think unicorns exist
2. Science has no evidence about unicorns.
3. Science therefore cannot prove if unicorns do or do not exist.
4. One day my friend, a very trustworthy person, said she saw a unicorn in the field by her house. There is no other evidence, other than the fact that my friend saw it.
5. Unicorns exist and any scientist who tries to deny the existence of unicorns is a fun-sucking, hostile human being.

The dialogue above features many key characteristics of Pseudo-Science. The speaker makes his or her point valid though the two facts alone that her friend had a personal experience and that science has no proof to prove the theory wrong. Finally, the speaker insults anyone who would challenge the theory. In science, challenges to a theory are accepted as everyone has the same common goal of improving the understanding of the natural word. Below is a table that lays out the key characteristics of Science and Pseudo-Science

SCIENCE	PSEUDO-SCIENCE
Science never proves anything.	Pseudoscience aimes to prove an idea.
Self-correcting methodology which involves critical thinking.	Starts with a conculsion and gives easy answers to complex problems.
An on-going process to develop a better understanding of the physical world by testing all possible hypotheses.	Often driven by social, political or commercial goals.
Involves a continual expansion of knowledge due to intense research.	A field has not evolved a lot since the beginning. If any research is done, it is done to justify the claims, rather that expand them.
Scientists constantly attempt to refute other scientists' works.	An attempt to disprove the beliefs is considered hostile and unacceptable.
When results or observations are not consistent with a scientific understanding, intense research follows.	Results or observations that are not consistent with current beliefs are ignored.
Remains questionable at any time. There are two types of theories: those that have been proven wrong by experimentation and data, and every other theory. Thus, no theory can be proven correct; every theory is also subject to being refuted.	Beliefs of the field can not usually be tested empirically so will likely not ever be proven wrong; Thus, Pseudo-scientists believe that they are right just because no one can prove them wrong.
Concepts are based on previous understandings or knowledge.	Pseudo-Scientists are often not in touch with main-stream science and are often driven by the egos of the "scientists". Furthermore, famous names and testimonials are often used for support rather than scientific evidence.
Findings must be stated in unambiguous, clear language.	Pseudoscience often uses very vague, yet seemingly technical terms.

Phrenology



Phrenology, also known as craniology, was a "science" popular during the early 1800s that was centered around the idea that the brain was an organ of the mind. During this time, most people believed that the brain was divided into distinct sections that all controlled different parts of a person's personality or intelligence. The basis of phrenology revolves around the concept that the brain mirrors a muscle and those parts of the brain which are "exercised" the most, will be proportionally larger than those parts of the brain that aren't often used. Thus, the scientists pictured the brain as a bumpy surface, with the make-up of the surface differing for every person depending on their personality and intelligence. By the mid 19th century, automated phrenology machines existed, which was basically a set of spring loaded probes that were placed on the head to measure the topography of one's skull. The machine then gave an automated reading about a person's characteristics based on this.

Let's consider some of the key characteristics of pseudo-science from our chart, and see how they apply to phrenology.

- Pseudo-Scientists are often not in touch with main-stream science: Scientific research has since the 1800s shown how though the brain is indeed divided into sections, each section does not determine a characteristic or personality trait, but instead controls a specific function such as memory or motor skills. Likewise, it has been concluded that the brain conforms to the shape of the skull , rather than the skull conforming to the shape of the brain (meaning the bumps of a persons skull have nothing to do with the shape of the brain). Back in the 1800s, little knowledge existed about the realities of brain structure and function, so the concept wasn't as reflexive of pseudo-science as it is today. However, some doctors and scientist still believe in the basic tenets of phrenology. Phrenology today exists as a classic form of pseudo-science as it goes against the common understanding about how the brain functions.
- Often driven by social, political or commercial goals- Indeed, the main goal of phrenology was a political and social one: to prove the dominance of the white race over other races. "Scientists" measured the brains of both races and concluded that the

brains of white people were larger then that of people of African descent. Therefore, they concluded, they were smarter and superior. It was later revealed that the scientists were biased while conducting the experiment and that they were previously aware of what race each brain belonged to. The experiment was repeated and this time the scientists were not aware of the race and they concluded that the brains were of equal size. The second experiment better conforms to the scientific method, as in this case the scientists objectively measured the brains, while in the first case the bias of the scientists lead to their conclusions. Thus, this situation demonstrates a two-fold level of defective science because not only was the idea of measuring the brains to determine personality and intelligence not correct all together, but the methods in which the scientists were doing this was also flawed. Phrenology was also commercially driven, since phrenology parlors where very wide spread and many devices were on the market to be used to measure.

- Pseudo-Scientists are often driven by the egos of the "scientists"- In the book *Phrenology and the origins of Victorian Scientific Naturalism* by John Van Whye, Van Whye quotes about the main discoverer of Phrenology Franz Joseph Gall, that " the peculiar incentive behind Gall's fascination with explaining individuals' differences may have lain in his hubris" (Van Whye 18). Of the 12 children in his family, Gall was the sharpest and brightest and naturally interested in distinguishing factors between children. Even as a young school boy, Gall noticed that the other children who were just as good at memorization as he was all had protruding eyes, which lead him to the idea of the basis of phrenology, that the characteristics of one's head indicates his or her intelligence.

Reflexology

Reflexology is a way of treatment that involves physically applying pressure to the feet or hands with the belief that each are divided up into different zones that are "connected" to other parts of the body. Thus, reflexologists assert that they can make physical changes throughout the body simply by rubbing ones hands or feet. Like we did with phrenology, lets go through some of the main characteristics of Pseudo-Science and see how they apply to reflexology.

- Pseudo-Scientists are often not in touch with main-stream science: No Scientific research has proven the validity of reflexology and how in fact it would actually work. In 2009, the Australian Medical Journal conducted an extensive study on reflexology and concluded "The best evidence available to date does not demonstrate convincingly that reflexology is an effective treatment for any medical condition". However, despite this lack of evidence, Reflexology continues.
- Pseudoscience often uses very vague, yet seemingly technical terms terms A main focus of reflexology is that the pressure on the foot removes any blockage of Qi, the "life energy force" and restores balance to lead to better health. Terms like "vital energy" or "energy blockage" which are used to talk about reflexology are classic pseudo-science terms; they sound impressive yet have no meaning to us
- Furthermore, famous names and testimonials are often used for support rather than scientific evidence. Because pseudo-science beliefs do not use scientific data for support, they must rely on individual circumstances when their product, idea, etc. appeared to have worked. For example, on the home page of well-known reflexologist Laura Norman's home page, she has a quote of Regis Philben (past host of W*ho Wants to be a Millionaire?*) saying "Laura Norman's Reflexology spared me from a kidney stone operation and saved my life.", opposed to a quote from say, a medical journal, that would cite how many studies say reflexology is an extremely effective form of treatment.

Distinguishing Pseudo-Science from other types of invalid science

An important distinction should be made between Pseudo-science and other types of defective science. Take for example, the "discovery" of N-rays. While attempting to polarize X-rays, physicist René Prosper Blondlot claimed to have discovered a new type of radiation he called N-rays. After Blondlot shared with others his exciting discovery, many other scientists confirmed his beliefs by saying they too had saw the N-rays. Though he claimed N-rays contained impossible properties, Blondlot asserted when he put a hot wire in an iron tube, he was able to detect the N-rays when he used a thread of calcium sulfite that glowed slightly when the rays were sent through a prism of aluminum. Blondlot claimed that all substances except some treated metals and green wood emit N-rays. However, Nature magazine was skeptical of Blondlot and sent physicist Robert Wood to investigate. Before Blondlot was about to show Wood the rays, Wood removed the aluminum prism from the machine without telling Blondlot. Without the prism, the rays would be impossible to detect. However, Blondlot claimed to still see the N-rays, demonstrating how the N-rays did not exist; Blondlot just wanted them to exist. This is an example of Pathological science, a phenomenon which occurs when scientists practice wishful data interpretation and come up with results they want to see. This case of Pathological

science and Pseudo-science differ. For one, Blondlot asked for a confirmation by other experts, something Pseudo-science usually lacks. More importantly, in pathological science, a scientist starts by following the scientific method; Blondlot was indeed doing an experiment when he made his discovery and proceeded to experiment when he found the substances that did not emit the rays. However, Pseudo-science usually includes a complete disregard of the scientific method, while Pathological scientists includes following the scientific method but seeing the results you wish to see.

Another type of invalid science, called hoax science occurred in 1999 when a team at the Lawrence Berkeley National Laboratory claimed to have discovered elements 116 and 118 when they bombarded Lead with Krypton particles. However, by 2002 it had been discovered that physicist Victor Ninov had intentionally fudged the data to get the ideal results. Thus, the concept of hoax science, which occurs when the data is intentionally falsified, differs both from pathological and pseudo science. In pathological science, scientists wishfully interpret the data and legitimately think they see what they want to see. However, in Hoax science, scientists know they don't see what they want to see, but just say they did. Finally, in Pseudo-Science, scientists don't consider the scientific method at all as they don't use valid experiments to back up their data in the first place.

From Pseudo-Science to Science

There have been incidents where what was once considered pseudo-science became a respectable theory. In 1911, German astronomer and meteorologist Alfred Wegener first began developing the idea of Continental Drift. The observation that the coastlines of African and South American seemed to fit together was not a new observation: scientists just couldn't believe that the continents could have drifted so far to cross the 5,000 mile Atlantic Ocean. At the time, it was a common theory that a land bridge had existed between Africa and Brazil. However, one day in the library Wegener read a study about a certain species that could not have crossed the ocean, yet had fossils appeared on both sides of the supposed land bridge. This piece of evidence lead Wegener to believe that our world had once been one piece, and had since drifted apart. However, Wegener's theory encountered much hostility and disbelief. In this time, it was the norm for scientists to stay within the scopes of their fields, meaning biologists did not study physics, chemists did not study oceanology and of course, meteorologists/astronomers like Wegener did not study geology. Thus, Wegener's theory faced much criticism just due to the fact that he was not a geologist. Also, Wegener could not explain why the continents moved, just that they did. This lack of reasoning lead to more skepticism about the theory and all these factors combined lead to the viewing of continental drift as Pseudo-Science. However, today much evidence exists that shows that Continental Drift is a perfectly acceptable scientific theory. Today, the modern ideas of plate tectonics can help explain Continental Drift, as the Plate Tectonic Theory presents the idea that the earth's surface is made up of several large plates that often move up to a few inches every year. Also, the development of paleomagnetism, which allows us to determine the earth's magnetic poles at the time a rock formed, suggests that the earth's magnetic poles have changed many times in the last 175 million years and that at one time South America and Africa were connected.

Limitations of the Scientific Method

Due to the need to have completely controlled experiments to test a hypothesis, science can not prove everything. For example, ideas about God and other supernatural beings can never be confirmed or denied, as no experiment exists that could test their presence. Supporters of Intelligent Design attempt to convey their beliefs as scientific, but nonetheless the scientific method can never prove this. Science is meant to give us a better understanding of the mysteries of the the natural world, by refuting previous hypotheses, and the existence of supernatural beings lies outside of science all together. Another limitation of the scientific method is when it comes making judgements about whether certain scientific phenomenons are "good" or "bad". For example, the scientific method cannot alone say that global warming is bad or harmful to the world, as it can only study the objective causes and consequences. Furthermore, science cannot answer questions about morality, as scientific results lay out of the scope of cultural, religious and social influences.

Concept Assessment

Determine if each statement is true or false (see answers at bottom of the page)

1. What is considered Pseudo-Science today will always be considered Pseudo-Science
2. A person has a cold and decides to seek reflexology treatment. The next day, the person gets better. This means reflexology is a valid scientific theory
3. Just because "science" is immoral or defective does not necessarily mean it is Pseudo-Science

4. Famous people are used in advertisements for products such as gatorade. This means these products are Pseudo-Science
5. Medically based Pseudo-Science such as homeopathy, reflexology or acupuncture have absolutely no benefits to people

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Answers to concept assessment

1. False- just because something is considered pseudo-science today, does not mean it will always be. Take for example, our discussion about Continental Drift. Continental Drift used to be considered Pseudo-Science, but now since there is scientific evidence to prove it, the theory is considered a product of science.
2. False- Just because a person got better after having reflexology treatment does not mean the treatment, which has no scientific evidence behind it, is the sole reason for a person's recovery. Many other factors could have lead to a person's healing, such as medication or time to let the body fight by itself so it would be impossible to determine that reflexology caused a person to get over a cold
3. True- Pseudo-Science is a specific type of defective. See the discussion about pathological and hoax science to learn how to distinguish Pseudo-Science from other types of invalid Science.
4. False- The common characteristic of relying on testimonials or celebrity support of Pseudo-Science is just one of the many characteristics on Pseudo-Science. Before declaring something as Pseudo-Science or science, it is important to consider various characteristics of both and focus on whether or not the ideas have experimentally determined data to support them. There has indeed been Scientific Data to support the use of Gatorade.
5. False- though there is little scientific evidence to support these types of medical treatment, it does not mean that they have no value. The Placebo effect may be relevant here, as people may believe that the methods are working, which may trigger the body to actually feel better.

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1.6.2: Using the Scientific Method

Learning Objectives

- To identify the components of the scientific method
- Classify measurements as being quantitative or qualitative.
- Evaluate science in the media.

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 **1.6.2.1**).

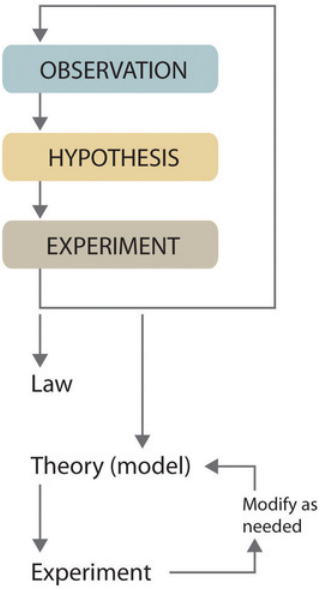


Figure **1.6.2.1**: The Steps in the Scientific Method. (CC BY-SA-NC; anonymous).

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—whose chemical name is sodium chloride—dissolves 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 corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

a. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
b. the sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the 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 support or refute 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 which case he can proceed to step 5. In other cases, experiments often demonstrate that the hypothesis is incorrect or that it must be modified thus requiring further experimentation.

Step 5: Development into 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 law, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the law of definite proportions, which was 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, and 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. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered.

Because scientists can enter the cycle shown in Figure **1.6.2.1** 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.

A Real-World Application of the Scientific Method

In 2007, my husband and I journeyed to China to adopt our daughter. Upon arrival in Beijing, I became violently ill. Due to her visa paperwork, my husband, daughter, and I were required to stay in China for two weeks. Unfortunately, I was ill the entire time. Once the two-week period was up, the three of us flew back to the United States where I continued to be sick. For the next year, I remained ill and lost a total of 30 pounds. The picture below shows me holding my daughter eight months after we returned home from China.



Figure **1.6.2.2**: Mother and child. (CC BY-SA-NC; Elizabeth R. Gordon).

I would like you to attempt to perform the scientific method on my situation described above. List the steps of the scientific method along with some plausible explanations. * **Please have this ready to discuss in class**.*

Exercise \(\PageIndex{2}\)

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

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really “consumes 47 times its weight in excess stomach acid.”
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.
d. Michael Jordan is the greatest pure shooter ever to play professional basketball.
e. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
f. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

Answer a

experiment

Answer b

law

Answer c

theory

Answer d

hypothesis

Answer e

qualitative observation

Answer f

quantitative observation

Evaluating Science in the Media

A Rough Guide to

SPOTTING BAD SCIENCE

Being able to evaluate the evidence behind a scientific claim is important. Being able to recognise bad science reporting, or faults in scientific studies, is equally important. These 12 points will help you separate the science from the pseudoscience.

1. SENSATIONALISED HEADLINES

Article headlines are commonly designed to entice viewers into clicking on and reading the article. At times, they can over-simplify the findings of scientific research. At worst, they sensationalise and misrepresent them.

2. MISINTERPRETED RESULTS

News articles can distort or misinterpret the findings of research for the sake of a good story, whether intentionally or otherwise. If possible, try to read the original research, rather than relying on the article based on it for information.

3. CONFLICTS OF INTEREST

Many companies will employ scientists to carry out and publish research - whilst this doesn't necessarily invalidate the research, it should be analysed with this in mind. Research can also be misrepresented for personal or financial gain.

4. CORRELATION & CAUSATION

Be wary of any confusion of correlation and causation. A correlation between variables doesn't always mean one causes the other. Global warming increased since the 1800s, and pirate numbers decreased, but lack of pirates doesn't cause global warming.

5. UNSUPPORTED CONCLUSIONS

Speculation can often help to drive science forward. However, studies should be clear on the facts their study proves, and which conclusions are as yet unsupported ones. A statement framed by speculative language may require further evidence to confirm.

6. PROBLEMS WITH SAMPLE SIZE

In trials, the smaller a sample size, the lower the confidence in the results from that sample. Conclusions drawn can still be valid, and in some cases small samples are unavoidable, but larger samples often give more representative results.

7. UNREPRESENTATIVE SAMPLES USED

In human trials, subjects are selected that are representative of a larger population. If the sample is different from the population as a whole, then the conclusions from the trial may be biased towards a particular outcome.

8. NO CONTROL GROUP USED

In clinical trials, results from test subjects should be compared to a 'control group' not given the substance being tested. Groups should also be allocated randomly. In general experiments, a control test should be used where all variables are controlled.

9. NO BLIND TESTING USED

To try and prevent bias, subjects should not know if they are in the test or the control group. In 'double blind' testing, even researchers don't know which group subjects are in until after testing. Note, blind testing isn't always feasible, or ethical.

10. SELECTIVE REPORTING OF DATA

Also known as 'cherry picking', this involves selecting data from results which supports the conclusion of the research, whilst ignoring those that do not. If a research paper draws conclusions from a selection of its results, not all, it may be guilty of this.

11. UNREPLICABLE RESULTS

Results should be replicable by independent research, and tested over a wide range of conditions (where possible) to ensure they are consistent. Extraordinary claims require extraordinary evidence - that is, much more than one independent study!

12. NON-PEER REVIEWED MATERIAL

Peer review is an important part of the scientific process. Other scientists appraise and critique studies, before publication in a journal. Research that has not gone through this process is not as reputable, and may be flawed.

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1.7: Chemistry in the Environment

Chemistry has been definced as the science that is concerned with the composition, properties, and structure of matter and with the ways in which substances can change from one form to another. But this definition is too broad to be useful. Chemistry isn't the only science that deals with the composition and transformations of matter. Matter in the environment is composed of clouds, whose transformations into rain snow are studied by meteorologists; it is composed of lakes studied by limnologists, or of trees which transform by processes studied by forresters. Chemists are unique because they understand or explain everything, even the subjects studied by all the scientists mentioned above, in terms of the properties of just over 100 kinds of atoms found in all matter, and the amazing variety of molecules that are created by forming and breaking bonds between atoms. ***So chemistry is defined by its approach, not its subject matter***. Chemistry explains or understands any subject in terms of the properties of atoms and molecules.

Exactly what we mean by a “chemical” needs to be explored, because environmentalists are often opposed to using "chemical" fertilizers, or "chemical" approaches to solving problems. If chemistry explains things in terms of atomic or molecular properties, a chemical must be something that is understood that way. In other words, we might call a glass of water a *nonchemical* if we just drink it, or a *chemical* if we drop a lump of sodium in it and want to explain the incredible reactivity of water, producing in this case hydrogen which may explode.

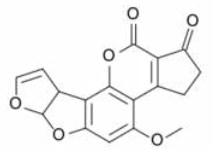


Water is not a chemical



Water is a Chemical

So laypeople who talk of “chemical free” natural foods, for example, are not necessarily at odds with chemists who claim “everything is made of chemicals”. When people speak of "chemical free" products, they usually mean that the material is found in nature and so did not require chemical knowledge to design or understand it. The very same molecule might be called a chemical under some circumstances. Chemists often say 'everything is a chemical" because it is possible to understand everything in terms of molecular properties, but of course anyone who pays attention to common language knows that that is not a meaningful thing to say. Very dangerous "chemicals" are made by natural processes (the strongest poisons known, and by understanding their molecular properties, chemists can learn how to control or destroy them. For example, aflatoxins found naturally in peanuts and other grains are possibly the strongest carcinogen known. Aflatoxin-producing members of *Aspergillus* are common and widespread in nature. They can colonize and contaminate grain before harvest or during storage [1].



A Natural Chemical Toxin

A chemical is generally a pure substance, comprised of just one kind of molecule (or atom), because the properties and behavior of the pure substance can be understood in terms of the properties of that molecule. But molecules identical to those found in all of nature can be synthesized in a laboratory, and they are identical in all respects to natural ones.

From ChemPRIME: 1.0: Prelude to Chemistry

References

1. ↑ en.Wikipedia.org/wiki/Aflatoxin

Contributors and Attributions

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1.8: Applying Properties - MSDS

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1.8.1: Applying Properties - MSDS

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1.8.1.01: Applying Properties - MSDS

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1.8.1.1: Applying Properties - MSDS/SDS

Learning Objectives

- Review physical and chemical properties.
- Know the purpose of a MSDS/SDS.
- Explain the bolded words on this page.

What is a MSDS/SDS?

A Material Safety Data Sheet (MSDS) or Safety Data Sheet (SDS) is designed to provide both workers and emergency personnel with the proper procedures for handling or working with a particular substance. MSDS's include information such as physical data (melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment, and spill/leak procedures. These are of particular use if a spill or other accident occurs.

The MSDS's are available from many sources such as the chemistry store, health and safety offices, material producing companies, etc. Any business or industry that has chemicals on site is required to have access to MSDS files for employers to be able to access at any time. If an employee is concerned about their exposure to chemicals, they can peruse an MSDS to obtain helpful information. Likewise, one could research household chemicals that could be dangerous to humans and animals. Many substances found around the home (pesticides, fuels, and cleaners) can be hazardous or harmless.

Safety Data Sheets Requirement Summary		
1	Identification	Product identifier, recommended use and restrictions on use, supplier contact information, emergency phone number
2	Hazard Identification	Classification (hazard class and category), label elements (including hazard pictogram, signal word, hazard statement and precautionary statements) and other hazards (e.g. thermal hazards).
3	Composition / Ingredients Information	For a hazardous product that is a substance: the chemical name, synonyms, CAS No. and the chemical name of impurities, stabilizing solvents and stabilizing additives where classified and that contribute to the classification of the product. For a hazardous product that is a mixture: for ingredients that present a health hazard, the chemical name, synonyms, CAS No. and concentration. Note: Confidential Business Information Rules may apply.
4	First Aid Measures	First-aid measures by route of exposure as well as most important symptoms/effects.
5	Fire Fighting Measures	Suitable (and unsuitable) extinguishing media, specific hazards, special equipment and precautions for fire fighters.
6	Accidental Release Measures	Protective equipment, emergency procedures, methods and materials for containment and clean up.
7	Handling and Storage	Precautions for safe handling, conditions for storage, including any incompatibilities.
8	Exposure Controls / Personal Protection	Exposure limits, engineering controls, personal protective equipment.
9	Physical and Chemical Properties	Appearance, odour, odour threshold, pH, melting/freezing point, boiling point and range, flash point, upper and lower flammable or explosive limits.
10	Stability and Reactivity	Reactivity, chemical stability, possible hazardous reactions, conditions to avoid, incompatible materials, hazardous decomposition products.
11	Toxicological Information	Description of various toxic effects by route of entry, including effects of acute or chronic exposure, carcinogenicity, reproductive effects, respiratory sensitization.
12	Ecological Information	Aquatic and terrestrial toxicity (if available), persistence and degradability, bioaccumulative potential, mobility in soil
13	Disposal Considerations	Safe handling and methods of disposal, including contaminated packaging.
14	Transport Information	UN number and proper shipping name, hazard classes, packing group.
15	Regulatory Information	Safety, health and environmental regulations specific to the product.
16	Other Information	Other information, including date of the latest revision of the SDS.

Figure **1.8.1.1.1**: Categories of a MSDS/SDS document.

Other Terms Used in MSDS/SDS

Aspects of toxicity and how chemicals will affect a body can also be found in this resource. **Along with physical and chemical properties, you should be familiar with the terms below that could also be found in an MSDS/SDS document.**

- **Mutagen:** able to alter DNA and could result in carcinogenesis (a chemical example would be nitrosamine)
- **Carcinogen:** able to cause cancer (this can get complicated, animal and human carcinogens both exist). There are very few chemicals classified as being human carcinogens. (benzene, radon, asbestos)
- **Neurotoxin:** affects the nervous system (chemical examples include lead and mercury)

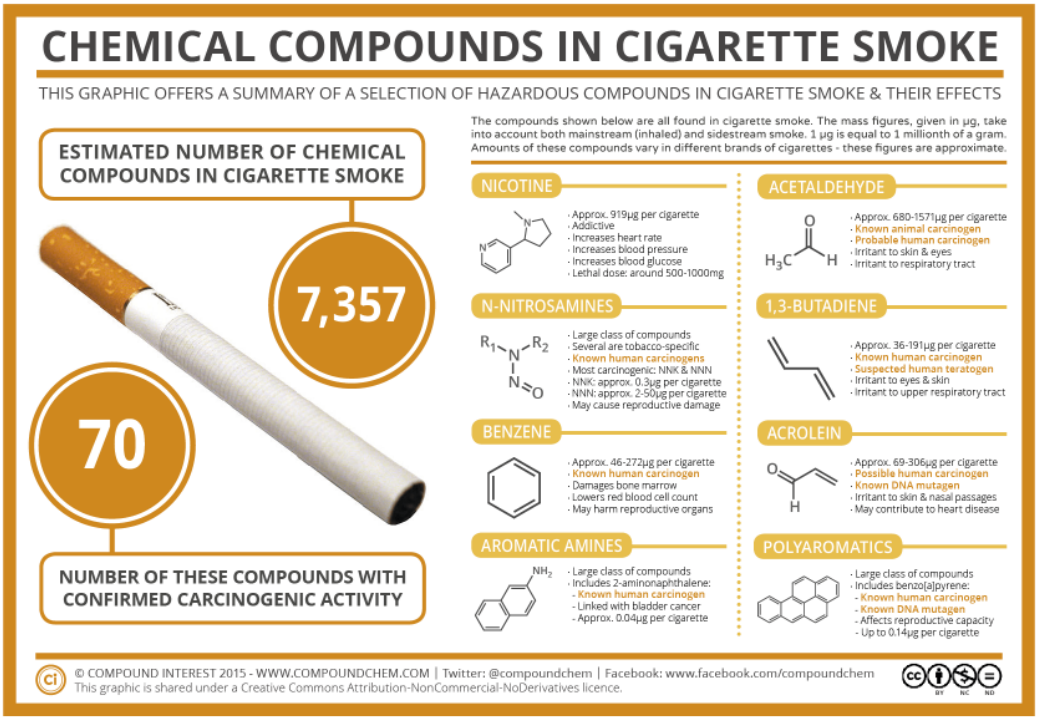


Figure **1.8.1.1.2**: Chemical Compounds in Cigarette Smoke. (CC-BY-NC-ND; Andy Brunning).

- **Teratogen**: affects developing fetus or embryo (pharmaceutical examples would be thalidomide and Accutane)
- **Corrosive**: can chemically destroy things easily (acids/bases are examples)
- **Flammable/Combustible**: able to catch on fire (examples would include gasoline and acetone)
- **Volatile**: a liquid that can transform into gas easily (examples would include gasoline and acetone)
- **LD50:** lethal dose (ingest,inhale, or inject) to kill 50% of a studied population (toxicology terminology)

MSDS/SDS's can be several pages long. A complete MSDS/SDS guide for acetic acid (also known as vinegar) can be viewed by clicking on this here. Although this chemical might appear dangerous, it used in the production of vinegar, ketchup, and barbeque sauce. *After looking over vinegar's entire MSDS/SDS sheet, write down any questions for your instructor regarding unfamiliar terminology.*

Exercise 1.8.1.1.1

After looking at the MSDS for acetic acid, answer the questions below:

a. Is this chemical a carcinogen?
b. Does acetic acid react with metals?
c. What odor does acetic acid produce?
d. If this chemical is ingested, should you induce vomiting to remove it from the body?
e. Does this chemical have a color?

Answer a

Acetic acid is not a carcinogen. It will not alter cause cancer.

Answer b

Acetic acid reacts with metals. This is a chemical property of this substance.

Answer c

Acetic acid smells like vinegar.

Answer d

Acetic acid is very corrosive and will eat biological tissues. If swallowed, vomiting should not be induced.

Answer e

This chemical is colorless



Figure **1.8.1.1.3**: IARC's carcinogenic classifications. (CC-BY-NC-ND, Andy Brunning)

? Exercise 1.8.1.1.1

Read over the cigarette infographic and write down all the chemicals listed that are known human carcinogens. Research chemicals used in vapes and record these on a sheet of paper. Using the MSDS/SDS toxicological section for each chemical, record all known human carcinogens in vapes.

Answer

For traditional cigarettes, aromatic amines, nitrosamines, benzene, acetaldehyde, 1,3-butadiene, and polyaromatics. For vapes, this will vary and we will discuss this in class.

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1.9: Alchemy

A common area of technology to societies of the past was metallurgy. Useful tools could be made with metallurgy that would last for a long time. Weapons could stay sharp longer with improved metals. Precious metals, such as gold and silver, could be refined and used for jewelry or for money. Because it was fairly rare, gold was considered to be very valuable, and became a common means of paying for goods and services.

However, mining for gold is a slow, dirty, and dangerous process. Not everyone owns a gold mine—in both the ancient Egyptian society and during the Roman Empire, the gold mines were the property of the state, not an individual or group. There were few ways for most people to legally get any gold for themselves.

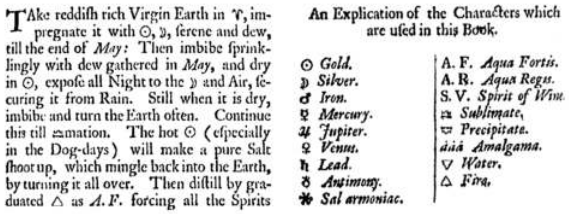
Alchemy

Chemistry is a subject that has its roots in the ancient tradition known as alchemy, from which it derives its name. Alchemy was a combination of philosophy and science that had both practical and mystical aspects. The goals of alchemy were varied and difficult to summarize. In many ways, the alchemists sought to achieve perfection, through such actions as the pursuit of the philosopher's stone and the elixir of life (Figure below). The philosopher's stone, it was believed, was a substance that was capable of being used to turn base metals (such as lead) into gold. It was also believed that it could be used to achieve rejuvenation and perhaps immortality. While alchemists did not ultimately succeed in these quests, their work provided the foundation for the modern study of chemistry.



Figure **1.9.1**: This painting by Joseph Wright (1771) is titled "The Alchymist, In Search of the Philosopher's Stone." (Public Domain; Joseph Wright of Derby / Derby Museum and Art Gallery via https://commons.wikimedia.org/wiki/F..._Alchemist.jpg)

Many of the specific approaches that alchemists used when they tried changing lead into gold are vague and unclear. Each alchemist had their own code for recording data. The processes were kept secret so that others could not profit from them. Different scholars developed their own set of symbols as they recorded the information they came up with. Many alchemists were not very honest, and sometimes took advantage of noblemen by taking money and claiming to be able to make gold from lead, then left town in the middle of the night. On occasion, the nobleman would detect the fraud and have the alchemist hung. By the 1300s, several European rules had declared alchemy to be illegal, and set out strict punishments for those practicing the alchemical arts.



TAke reddish rich Virgin Earth in ♈, impregnate it with ☉, ☽, ſerene and dew, till the end of *May*: Then imbibe ſprinklingly with dew gathered in *May*, and dry in ☉, expoſe all Night to the ☽ and Air, ſecuring it from Rain. Still when it is dry, imbibe and turn the Earth often. Continue this till ƒermation. The hot ☉ (eſpecially in the Dog-days) will make a pure Salt ſhoot up, which mingle back into the Earth, by turning it all over. Then diſtill by graduated △ as *A. F.* forcing all the Spirits

An Explication of the Characters which are uſed in this Book.

☉ *Gold.*
☽ *Silver.*
♂ *Iron.*
☿ *Mercury.*
♃ *Jupiter.*
♀ *Venus.*
♄ *Lead.*
♁ *Antimony.*
✻ *Sal armoniac.*

A. F. *Aqua Fortis.*
A. R. *Aqua Regis.*
S. V. *Spirit of Wine.*
♎ *Sublimate,*
♒ *Precipitate.*
ana Amalgama.
▽ *Water.*
△ *Fire.*

Figure **1.9.2**: Alchemist recipe. (Public Domain; Kenelm Digby via Wikipedia)

Alchemist Contributions to Chemistry

Alchemists laid the groundwork for many chemical processes, such as the refining of ores, the production of gunpowder, the manufacture of glass and ceramics, leather tanning, and the production of inks, dyes, and paints. Alchemists also made the first attempts at organizing and classifying substances so that they could better understand their reactions and be able to predict the products of their experiments. This eventually led to the modern periodic table, which you will learn about in a later chapter. Alchemy began to fully evolve into chemistry in the 17th century, with a greater emphasis on rational thought and experimentation and less emphasis on spirituality and mysticism.

The alchemists were never successful in changing lead into gold, but modern nuclear physics can accomplish this task. Lead is subjected to nuclear bombardment in a particle accelerator. A small amount of gold can be obtained by this process. However, the cost of the procedure is far more than that of the amount of gold obtained. So, the dream of the alchemists has never (and will never) come true.



Summary

- Gold has been considered valuable by all civilizations.
- The alchemists tried to find the philosopher's stone that would allow them to make gold from lead.
- The alchemists did not successfully transform lead into gold.
- The alchemists laid the ground work for many advances to the new science of chemistry.

Review

1. Why is gold considered to be valuable?
2. Who owned the gold mines during the ancient Egyptian and Roman civilizations?
3. What is the elixir of life?
4. What contributions to modern chemistry were made by the alchemists?

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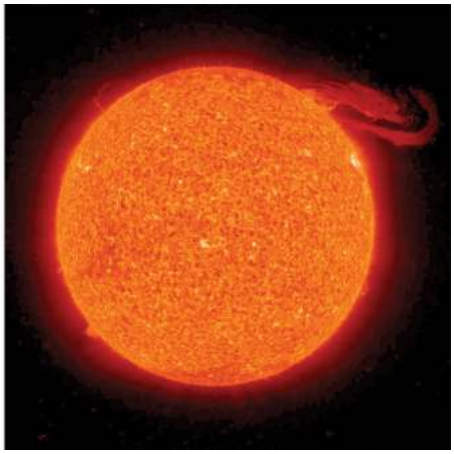
CHAPTER OVERVIEW

2: Atoms, Molecules, and Ions

Although not an SI unit, the angstrom (Å) is a useful unit of length. It is one ten-billionth of a meter, or 10^{-10} m. Why is it a useful unit? The ultimate particles that compose all matter are about 10^{-10} m in size, or about 1 Å. This makes the angstrom a natural—though not approved—unit for describing these particles.

The angstrom unit is named after Anders Jonas Ångström, a nineteenth-century Swedish physicist. Ångström's research dealt with light being emitted by glowing objects, including the sun. Ångström studied the brightness of the different colors of light that the sun emitted and was able to deduce that the sun is composed of the same kinds of matter that are present on the earth. By extension, we now know that all matter throughout the universe is similar to the matter that exists on our own planet.





Anders Jonas Ångstrom, a Swedish physicist, studied the light coming from the sun. His contributions to science were sufficient to have a tiny unit of length named after him, the angstrom, which is one ten-billionth of a meter.

Source: Photo of the sun courtesy of NASA's Solar Dynamics Observatory.

2.1: Introduction to Atoms and Molecules
2.2: Basic Atomic Theory
2.3: Atomic Theory
2.4: Indivisible - The Atomic Theory
2.5: Isotopes and Atomic Mass
2.6: Quantum Numbers for Electrons
2.7: Organization of Electrons in Atoms
2.7.1: Atomic Models of the Twentieth Century
2.8: Electronic Structure and the Periodic Table

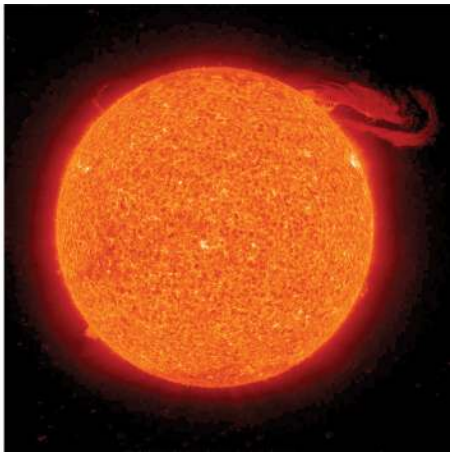
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2.1: Introduction to Atoms and Molecules

Although not an SI unit, the angstrom (Å) is a useful unit of length. It is one ten-billionth of a meter, or 10^{-10} m. Why is it a useful unit? The ultimate particles that compose all matter are about 10^{-10} m in size, or about 1 Å. This makes the angstrom a natural- though not approved-unit for describing these particles.

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2.2: Basic Atomic Theory

Learning Objectives

- Give a short history of the concept of the atom.
- Describe the contributions of Democritus and Dalton to atomic theory.
- Summarize Dalton's atomic theory and explain its historical development.

Democritus and the Greek Philosophers

Around 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, big, unchangeable "thing." Democritus was one of the first people to propose the term "atoms." 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 **2.2.1**: 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.

Early Greek philosophers tried to understand the nature of the world through reason and logic, 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 many 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 many discoveries that they could have made otherwise. Greek philosophers dismissed Democritus' theory entirely. Unfortunately, it took over two millennia before the theory of atomos (or "atoms," as they're known today) was fully accepted.



Video **2.2.1**: Since ancient Greek times, philosophers and scientists have tried to figure out what an atom looks like. For a couple thousand years, humans could only speculate on the structure and other properties of the smallest unit of matter. It wasn't until the 1980s that chemists could see individual atoms. Bestselling author Sam Kean takes us through the nearly 2,400-year quest to see the atom in a new episode of the "Legends of Chemistry" series.

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 1800's with the work of the British

scientists 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.

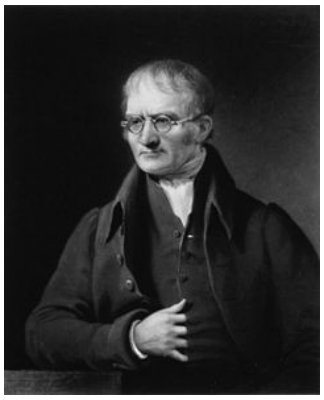


Figure **2.2.3**: British physicist and chemist John Dalton (1766-1844). Unlike the greek philosophers, John Dalton believed in both logical thinking and experimentation.

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

From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the atom (1803). This later became known as Dalton's **atomic theory**. The published (1808) tenets of this theory were as follows:

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

Dalton's Eyes

As a scientist, John Dalton was also interested in colorblindness. Both he and his brother suffered from red/green colorblindness. At this time (1794), no other scientist had explored this medical issue. He devised theories (although not correct) as to why he could not differentiate between red and green. In addition, he named this medical condition "Daltonism." Upon his death (1844), he donated his eyes to a medical research facility in Manchester, England. Today, his eyes are still on display at the Museum of Science and Industry in Manchester, England.



Figure **2.2.3**: Image taken from: https://c1.staticflickr.com/3/2823/1...37dd23af_b.jpg

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, atoms can even be used for making pretty images or as IBM research demonstrate in Video **2.2.2**, control of individual atoms can be use used create animations. 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.

Video **2.2.2**: A Boy And His Atom: The World's Smallest Movie

Dalton was not completely correct

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We know now that:

1. An atom is composed of smaller particles (electrons, protons, and neutrons).
2. All atoms of an element are not identical. The existence of isotopes illustrates this phenomena.
3. Through the use of nuclear reactions, atoms of one element can be changed into atoms of another element.

The first two will be be discussed later in this chapter, while the last requires introducing "nuclear chemistry" and will be discussed in a different chapter.

References

1. https://pubs.acs.org/subscribe/archi...3chemchron.pdf

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2.3: Atomic Theory

Learning Objectives

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

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

The concept that atoms play a fundamental role in chemistry is formalized by the modern atomic theory, first stated by John Dalton, an English scientist, in 1808. It consists of three parts:

1. All matter is composed of atoms.
2. Atoms of the same element are the same; atoms of different elements are different.
3. Atoms combine in whole-number ratios to form compounds.

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called *subatomic particles*. The first part to be discovered was the electron, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The proton is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The neutron is a subatomic particle with about the same mass as a proton, but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table **2.3.1** summarizes the properties of these three subatomic particles.

Table **2.3.1**: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; kg)	Charge
Proton	p^+	1.6×10^{-27}	1+
Neutron	n, n^0	1.6×10^{-27}	none
Electron	e^-	9.1×10^{-31}	1−

How are these particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910s pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the nucleus of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure **2.3.1**).

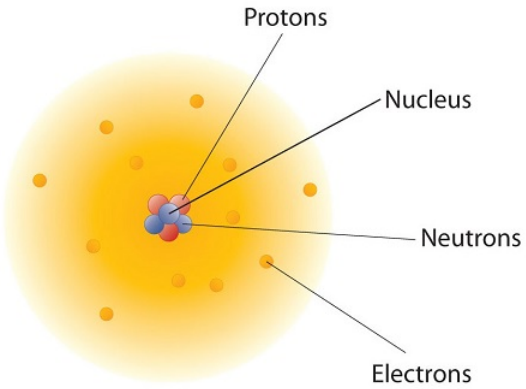


Figure **2.3.1**: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

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

Atoms of the same element can have different numbers of neutrons, however. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called isotopes. Most naturally occurring elements exist as isotopes. For example, most hydrogen atoms have a single proton in their nucleus. However, a small number (about one in a million) of hydrogen atoms have a proton and a neutron in their nuclei. This particular isotope of hydrogen is called deuterium. A very rare form of hydrogen has one proton and two neutrons in the nucleus; this isotope of hydrogen is called tritium. The sum of the number of protons and neutrons in the nucleus is called the mass number of the isotope.

Neutral atoms have the same number of electrons as they have protons, so their overall charge is zero. However, as we shall see later, this will not always be the case.

✔ Example 2.3.1

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

Solution

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

? Exercise 2.3.1

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

When referring to an atom, we simply use the element's name: the term *sodium* refers to the element as well as an atom of sodium. But it can be unwieldy to use the name of elements all the time. Instead, chemistry defines a symbol for each element. The atomic symbol is a one- or two-letter representation of the name of an element. By convention, the first letter of an element's symbol is always capitalized, while the second letter (if present) is lowercase. Thus, the symbol for hydrogen is H, the symbol for sodium is Na, and the symbol for nickel is Ni. Most symbols come from the English name of the element, although some symbols come from an element's Latin name. (The symbol for sodium, Na, comes from its Latin name, *natrium*.) Table **2.3.2** lists some common elements and their symbols. You should memorize the symbols in Table **2.3.2**, as this is how we will be representing elements throughout chemistry.

Table **2.3.2**: Names and Symbols of Common Elements

Element Name	Symbol	Element Name	Symbol
Aluminum	Al	Mercury	Hg
Argon	Ar	Molybdenum	Mo
Arsenic	As	Neon	Ne
Barium	Ba	Nickel	Ni
Beryllium	Be	Nitrogen	N
Bismuth	Bi	Oxygen	O
Boron	B	Palladium	Pd
Bromine	Br	Phosphorus	P
Calcium	Ca	Platinum	Pt
Carbon	C	Potassium	K
Chlorine	Cl	Radium	Ra
Chromium	Cr	Radon	Rn
Cobalt	Co	Rubidium	Rb
Copper	Cu	Scandium	Sc
Fluorine	F	Selenium	Se
Gallium	Ga	Silicon	Si
Germanium	Ge	Silver	Ag
Gold	Au	Sodium	Na
Helium	He	Strontium	Sr
Hydrogen	H	Sulfur	S
Iodine	I	Tantalum	Ta
Iridium	Ir	Tin	Sn
Iron	Fe	Titanium	Ti
Krypton	Kr	Tungsten	W
Lead	Pb	Uranium	U
Lithium	Li	Xenon	Xe
Magnesium	Mg	Zinc	Zn
Manganese	Mn	Zirconium	Zr

The elements are grouped together in a special chart called the periodic table of all the elements. A simple periodic table is shown in Figure **2.3.2**, while one may view a more extensive periodic table from another source. The elements on the periodic table are listed in order of ascending atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (Chapter 8). One immediate use of the periodic table helps us identify metals and nonmetals. Nonmetals are in the upper right-hand corner of the periodic table, on one side of the heavy line splitting the right-side part of the chart. All other elements are metals.

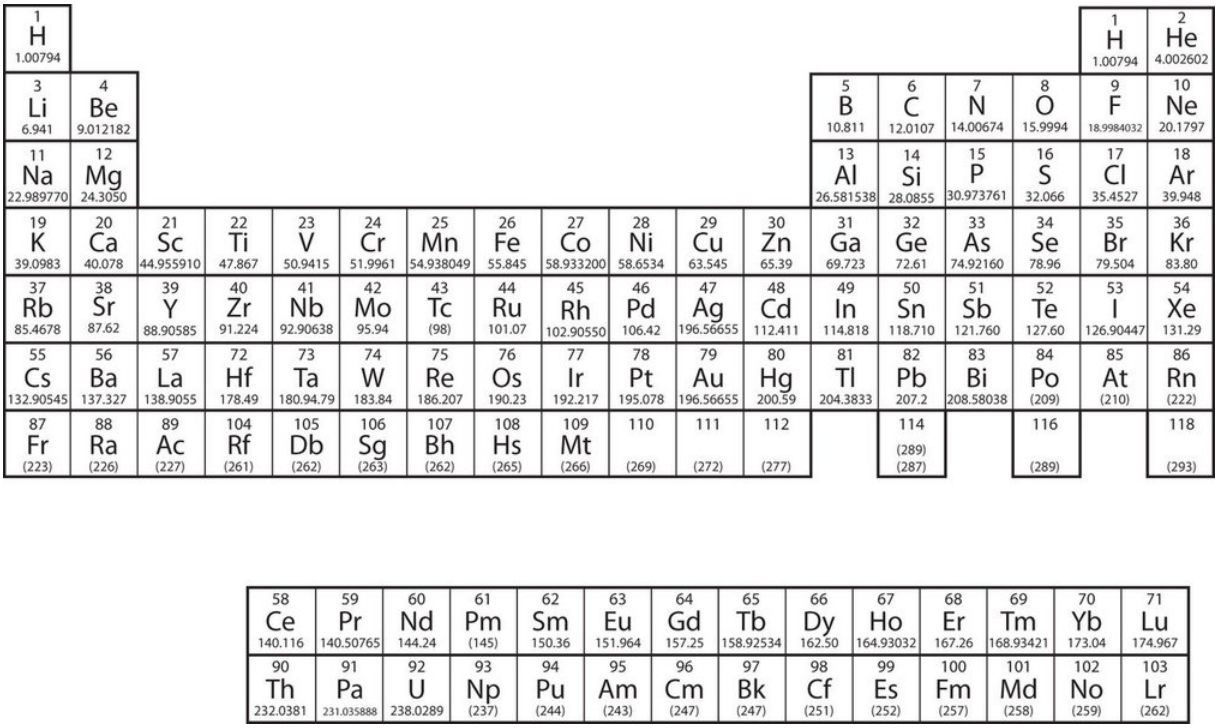


Figure 2.3.1: A Simple Periodic Table

There is an easy way to represent isotopes using the atomic symbols. We use the construction:

$$^{A}_{Z}X$$

where X is the symbol of the element, A is the mass number, and Z is the atomic number. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

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

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

Example 2.3.2

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?

b. How many protons and neutrons are in $^{56}_{26}Fe$

Solution

a. The symbol for this isotope is $^{235}_{92}U$

b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

Exercise 2.3.2

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

Answer

11 protons

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

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.
- The periodic table is a chart that organizes all the elements.

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2.4: Indivisible - The Atomic Theory

Learning Objectives

- Give a short history of the concept of the atom.
- Describe the contributions of Democritus and Dalton to atomic theory.
- Summarize Dalton's atomic theory and explain its historical development.

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, but 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, big, 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 **2.4.1**: (left) 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. (right) 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 are known today) was fully appreciated.

Greeks: "All Thought and No Action"

Greek philosophers were "all thought and no action" and did not feel the need to test their theories with reality. In contrast, Dalton's efforts were based on experimentation and testing ideas against reality.

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 1800's with the work of the British

scientists 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.

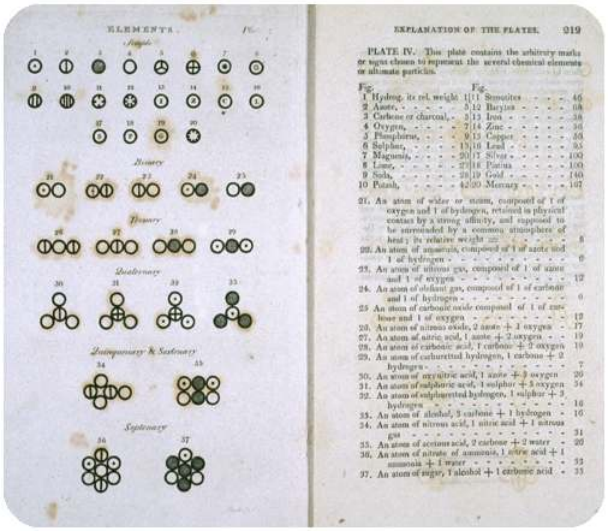
The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **2.4.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

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

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

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

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


ELEMENTS. IV.

EXPLANATION OF THE PLATES. 219

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Figure **2.4.2**: Dalton's symbols from his text "A New System of Chemical Philosophy."

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 **2.4.1**, control of individual atoms can be use used create animations.



Video **2.4.1**: 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

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

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2.5: Isotopes and Atomic Mass

Learning Outcomes

- Define atomic and mass numbers.
- Determine the number of protons, neutrons, and electrons in an atom.
- Identify the charge and relative mass of subatomic particles.
- Label the location of subatomic particles in the atom.
- Define isotope.
- Write the isotopic symbol of an atom.
- Explain the concept of average atomic mass.

Atoms are the fundamental building blocks of all matter and are composed of protons, neutrons, and electrons. Because atoms are electrically neutral, the number of positively charged protons must be equal to the number of negatively charged electrons. Since neutrons do not affect the charge, the number of neutrons is not dependent on the number of protons and will vary even among atoms of the same element.

Atomic Number

The **atomic number (Z)** *of an element is the number of protons in the nucleus of each atom of that element*. An atom can be classified as a particular element based solely on its atomic number. For example, any atom with an atomic number of 8 (its nucleus contains 8 protons) is an oxygen atom, and any atom with a different number of protons would be a different element. The periodic table (see figure below) displays all of the known elements and is arranged in order of increasing atomic number. In this table, an element's atomic number is indicated above the elemental symbol. Hydrogen, at the upper left of the table, has an atomic number of 1. Every hydrogen atom has one proton in its nucleus. Next on the table is helium, whose atoms have two protons in the nucleus. Lithium atoms have three protons, beryllium atoms have four, and so on.

Since atoms are neutral, the number of electrons in an atom is equal to the number of protons. Hydrogen atoms all have one electron occupying the space outside of the nucleus. Helium, with two protons, will have two electrons.

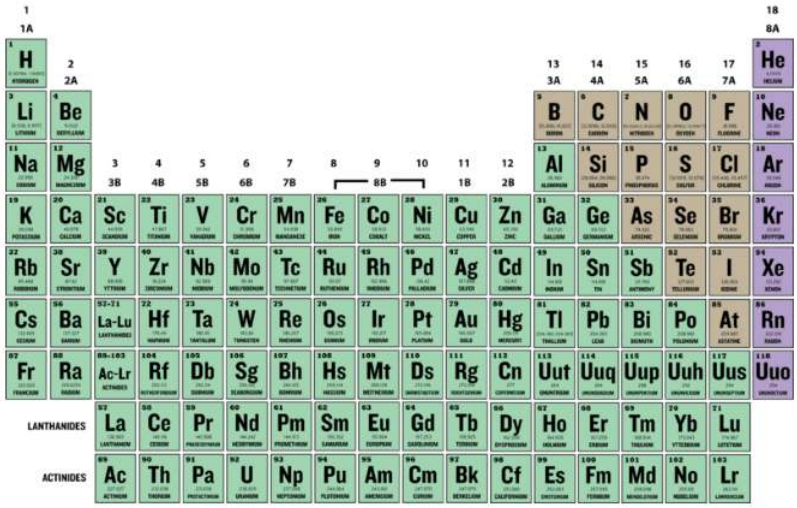


Figure **2.5.1**: The periodic table of the elements.

Mass Number

Experimental data showed that the vast majority of the mass of an atom is concentrated in its nucleus, which is composed of protons and neutrons. The **mass number** *is defined as the total number of protons and neutrons in an atom.* Consider the table below, which shows data from the first six elements of the periodic table.

Table **2.5.1**: Atoms of the First Six Elements

Name	Symbol	Atomic Number	Protons	Neutrons	Electrons	Mass Number
hydrogen	H	1	1	0	1	1
helium	He	2	2	2	2	4
lithium	Li	3	3	4	3	7
beryllium	Be	4	4	5	4	9
boron	B	5	5	6	5	11
carbon	C	6	6	6	6	12

View animations showing the atomic structure of the first 11 elements on the periodic table at http://web.visionlearning.com/custom...imations.shtml

Consider the element helium. Its atomic number is 2, so it has two protons in its nucleus. Its nucleus also contains two neutrons. Since $2 + 2 = 4$, we know that the mass number of the helium atom is 4. Finally, the helium atom also contains two electrons, since the number of electrons must equal the number of protons. This example may lead you to believe that atoms have the same number of protons and neutrons, but a further examination of the table above will show that this is not the case. Lithium, for example, has three protons and four neutrons, giving it a mass number of 7.

Knowing the mass number and the atomic number of an atom allows you to determine the number of neutrons present in that atom by subtraction.

$$\text{Number of neutrons} = \text{mass number} - \text{atomic number} \tag{2.5.1}$$

Atoms of the element chromium (Cr) have an atomic number of 24 and a mass number of 52. How many neutrons are in the nucleus of a chromium atom? To determine this, you would subtract as shown:

$$52 - 24 = 28 \text{ neutrons in a chromium atom} \tag{2.5.2}$$

The composition of any atom can be illustrated with a shorthand notation using the atomic number and the mass number. Both are written before the chemical symbol, with the mass number written as a superscript and the atomic number written as a subscript. The chromium atom discussed above would be written as:

$$^{52}_{24}\text{Cr} \tag{2.5.3}$$

Another way to refer to a specific atom is to write the mass number of the atom after the name, separated by a hyphen. The above atom would be written as chromium-52, with the mass number written after the name. The atomic number does not have to be included because all atoms of chromium have the same number of protons but can vary in the atomic mass.

Isotopes

As stated earlier, not all atoms of a given element are identical. Specifically, the number of neutrons in the nucleus can vary for many elements. As an example, naturally occurring carbon exists in three forms, which are illustrated in the figure below.

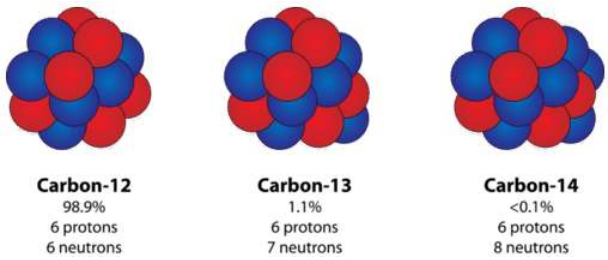


Figure 2.5.2: Nuclei of the three isotopes of carbon. Almost 99% of naturally occurring carbon is carbon-12, whose nucleus consists of six protons and six neutrons. Carbon-13 and carbon-14, with seven or eight neutrons, respectively, have a much lower nuclei abundance.

Each carbon atom has the same number of protons (6), which is equal to its atomic number. Each carbon atom also contains six electrons, allowing the atom to remain electrically neutral. However, the number of neutrons varies from six to eight. **Isotopes** *are atoms that have the same atomic number but different mass numbers due to a change in the number of neutrons.* The three isotopes of carbon can be referred to as carbon-12 ($^{12}_{6}C$), carbon-13 ($^{13}_{6}C$), and carbon-14 ($^{14}_{6}C$). Naturally occurring samples of most elements are mixtures of isotopes. Carbon has only three natural isotopes, but some heavier elements have many more. Tin has ten stable isotopes, which is the most of any known element. The nucleus of a given carbon atom will be one of the three possible isotopes discussed above.

While the presence of isotopes affects the mass of an atom, it does not affect its chemical reactivity. Chemical behavior is governed by the number of electrons and the number of protons. Carbon-13 behaves chemically in exactly the same way as the more plentiful carbon-12.

Size of Atoms

The graphite in your pencil is composed of the element carbon, a nonmetal. Imagine taking a small piece of carbon and grinding it until it is a fine dust. Each speck of carbon would still have all of the physical and chemical properties of carbon. Now imagine that you could somehow keep dividing the speck of carbon into smaller and smaller pieces. Eventually, you would reach a point where your carbon sample is as small as it could possibly be. This final particle is called an atom.

Atoms, as you probably know, are extremely small. In fact, the graphite in an ordinary pencil contains about 5×10^{20} atoms of carbon. This is an almost incomprehensibly large number. The population of the entire Earth is about 7×10^{9} people, meaning that there are about 7×10^{10} times as many carbon atoms in your pencil as there are people on Earth! For this to be true, atoms must be extremely small. We can only see atoms with a modern instrument called a scanning tunneling microscope. (www.nobelprize.org/educationa...opes/scanning/)

Atomic Mass

The masses of individual atoms are very, very small. However, using a modern device called a mass spectrometer, it is possible to measure such miniscule masses. An atom of oxygen-16, for example, has a mass of 2.66×10^{-23} g. While comparisons of masses measured in grams would have some usefulness, it is far more practical to have a system that will allow us to more easily compare relative atomic masses. Scientists decided on using the carbon-12 nuclide as the reference standard by which all other masses would be compared. By definition, one atom of carbon-12 is assigned a mass of exactly 12 atomic mass units (amu). An **atomic mass unit** *is defined as a mass equal to one twelfth of an atom of carbon-12*. The mass of any isotope of any element is expressed in relation to the carbon-12 standard. For example, one atom of helium-4 has a mass of 4.0026 amu. An atom of sulfur-32 has a mass of 31.972 amu.

The carbon-12 atom has six protons and six neutrons in its nucleus for a mass number of 12. Since the nucleus accounts for nearly all of the mass of the atom, a single proton or single neutron has a mass of approximately 1 amu. However, as seen by the helium and sulfur examples, the masses of individual atoms are not quite whole numbers. This is because an atom's mass is affected very slightly by the interactions of the various particles within the nucleus and also includes the small mass added by each electron.

As stated in the section on isotopes, most elements occur naturally as a mixture of two or more isotopes. Listed below (see table below) are the naturally occurring isotopes of several elements along with the percent natural abundance of each.

Table **2.5.2**: Atomic Masses and Percent Abundances of Some Natural Isotopes

Element	Isotope (Symbol)	Percent Natural Abundance	Atomic mass (amu)	Average atomic mass (amu)
Hydrogen	$^{1}_{1}H$	99.985	1.0078	1.0079
	$^{2}_{1}H$	0.015	2.0141	
	$^{3}_{1}H$	negligible	3.0160	
Carbon	$^{12}_{6}C$	98.89	12.000	12.011
	$^{13}_{6}C$	1.11	13.003	
	$^{14}_{6}C$	trace	14.003	
Oxygen	$^{16}_{8}O$	99.759	15.995	15.999
	$^{17}_{8}O$	0.037	16.995	
	$^{18}_{8}O$	0.204	17.999	
Chlorine	$^{35}_{17}Cl$	75.77	34.969	35.453
	$^{37}_{17}Cl$	24.23	36.966	
Copper	$^{63}_{29}Cu$	69.17	62.930	63.546
	$^{65}_{29}Cu$	30.83	64.928	

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

$$\frac{34.969 + 36.966}{2} = 35.968 \tag{2.5.4}$$

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

$$0.7577\,(34.969) + 0.2423\,(36.966) = 35.453 \tag{2.5.5}$$

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

Supplemental Resources

- Elements and Atoms: http://www.youtube.com/watch?v=IFKnq9QM6_A
- Introduction to the Atom: http://www.youtube.com/watch?v=1xSQIwWGT8M
- Atomic History - A Brief Discovery: http://www.pbs.org/wgbh/nova/diamond...dehistory.html
- All About Atoms: http://education.jlab.org/atomtour/index.html
- Build and Atom: http://phet.colorado.edu/en/simulation/build-an-atom
- Molecular Workbench - Atomic Structure: http://workbench.concord.org/databas...vities/47.html
- See Inside a Diamond: http://www.pbs.org/wgbh/nova/diamond/insidewave.html
- Isotopes and Atomic Mass: http://phet.colorado.edu/en/simulati...nd-atomic-mass

- Atomic Structure: freezeray.com/flashFiles/atomcStructure.htm
- Atom Builder: freezeray.com/flashFiles/atomBuilder.htm
- Tennis Ball Isotopes: http://www.youtube.com/watch?v=oLnuXpf4hsA
- Element Math Game: http://education.jlab.org/elementmath/index.html
- Atoms and Matter Crossword Puzzle: http://education.jlab.org/sciencecro.../atoms_01.html
- Atomic Number Review #1: www.sciencegeek.net/Chemistry...micNumbers.htm
- Atomic Number Review #2: www.sciencegeek.net/Chemistry...t1Numbers2.htm
- Atomic Structure: www.sciencegeek.net/Chemistry...omicStructure/

Contributors and Attributions

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2.6: Quantum Numbers for Electrons

Learning Objectives

- Explain what spectra are.
- Learn the quantum numbers that are assigned to electrons.

There are two fundamental ways of generating light: either heat an object up to be so hot that it glows, or pass an electrical current through a sample of matter (usually a gas). Incandescent lights and fluorescent lights generate light via these two methods, respectively.

A hot object gives off a continuum of light. We notice this when the visible portion of the electromagnetic spectrum is passed through a prism: the prism separates light into its constituent colors, and all colors are present in a continuous rainbow (Figure **2.6.1*a*** - Prisms and Light). This image is known as a **continuous spectrum**. However, when electricity is passed through a gas and light is emitted and this light is passed though a prism, we see only certain lines of light in the image (Figure **2.6.1*b***). This image is called a line spectrum. It turns out that every element has its own unique, characteristic line spectrum.



Figure **2.6.1**: Prisms and Light. (a) A glowing object gives off a full rainbow of colors, which are noticed only when light is passed through a prism to make a continuous spectrum. (b) However, when electricity is passed through a gas, only certain colors of light are emitted. Here are the colors of light in the line spectrum of Hg.

Why does the light emitted from an electrically excited gas have only certain colors, while light given off by hot objects has a continuous spectrum? For a long time, it was not well explained. Particularly simple was the spectrum of hydrogen gas, which could be described easily by an equation; no other element has a spectrum that is so predictable (Figure **2.6.2** - Hydrogen Spectrum). Late nineteenth century scientists found that the positions of the lines obeyed a pattern given by the equation

$$\frac{1}{\lambda} = (109,700 cm^{-1})\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where n = 3, 4, 5, 6, etc. However, they could not explain why this was so.

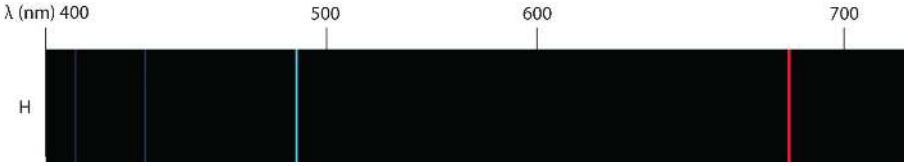


Figure **2.6.2**: Hydrogen Spectrum. The spectrum of hydrogen was particularly simple and could be predicted by a simple mathematical expression.

In 1913, the Danish scientist Niels Bohr suggested a reason why the hydrogen atom spectrum looked this way. He suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number n (the same n in the equation above and now called a **quantum number**). Quantities that have certain specific values are **quantized** values. Bohr suggested that the energy of the electron in hydrogen was quantized because it was in a specific orbit. Because the energies of the electron can have only certain values, the changes in energies can have only certain values (somewhat similar to a staircase—not only are the stair steps set at specific heights, but the height between steps is fixed). Finally, Bohr suggested that the energy of light emitted from electrified hydrogen gas was equal to the energy difference of the electron's energy states:

$$E_{light} = h\nu = \Delta E_{electron}$$

This means that only certain frequencies (and thus, certain wavelengths) of light are emitted. Figure **2.6.3** - Bohr's Model of the Hydrogen Atom, shows a model of the hydrogen atom based on Bohr's ideas.

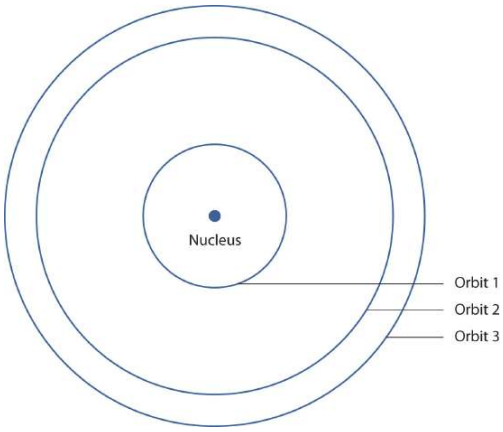


Figure **2.6.3**: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

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

In the quantum-mechanical model of an atom, the state of an electron is described by four quantum numbers, not just the one predicted by Bohr. The first quantum number is called the **principal quantum number(n).** The principal quantum number largely determines the energy of an electron. Electrons in the same atom that have the same principal quantum number are said to occupy an electron **shell** of the atom. The principal quantum number can be any nonzero positive integer: 1, 2, 3, 4,….

Within a shell, there may be multiple possible values of the next quantum number, the **angular momentum quantum number (ℓ)**. The ℓ quantum number has a minor effect on the energy of the electron but also affects the spatial distribution of the electron in three-dimensional space—that is, the shape of an electron's distribution in space. The value of the ℓ quantum number can be any integer between 0 and $n - 1$: $\ell = 0, 1, 2, \ldots, n - 1$.

Thus, for a given value of n, there are different possible values of ℓ:

Table with two columns and four rows. The first (left) column is labeled "If n equals" and the second (right) column is labeled "ℓ can be". Underneath the columns in the rows are different values. All of the rows have numerical values.

If *n* equals	ℓ can be
1	0
2	0 or 1
3	0, 1, or 2
4	0, 1, 2, or 3

and so forth. Electrons within a shell that have the same value of ℓ are said to occupy a **subshell** in the atom. Commonly, instead of referring to the numerical value of ℓ, a letter represents the value of ℓ (to help distinguish it from the principal quantum number):

Table with two columns and four rows. The first (left) column is labeled "If ℓ equals" and the second (right) column is labeled "The letter is". The rows underneath the left column are numbers and the rows underneath the right column are letters.

If ℓ equals	The letter is
0	*s*
1	*p*
2	*d*
3	*f*

The next quantum number is called the **magnetic quantum number (m_ℓ)**. For any value of ℓ, there are 2ℓ + 1 possible values of m_ℓ, ranging from −ℓ to ℓ:

$$-\ell < m\ell < \ell$$

or

$$|m_\ell| < \ell$$

The following explicitly lists the possible values of m_ℓ for the possible values of ℓ:

Table with two columns and four rows. The first (left) column is labeled "If ℓ equals" and the second (right) column is labeled "The mℓ values can be". The rows underneath the left column are positive numbers and the rows underneath the right column are negative numbers.

If ℓ equals	The m_ℓ values can be
0	0
1	−1, 0, or 1
2	−2, −1, 0, 1, or 2
3	−3, −2, −1, 0, 1, 2, or 3

The particular value of m_ℓ dictates the orientation of an electron's distribution in space. When ℓ is zero, m_ℓ can be only zero, so there is only one possible orientation. When ℓ is 1, there are three possible orientations for an electron's distribution. When ℓ is 2, there are five possible orientations of electron distribution. This goes on and on for other values of ℓ, but we need not consider any higher values of ℓ here. Each value of m_ℓ designates a certain orbital. Thus, there is only one orbital when ℓ is zero, three orbitals when ℓ is 1, five orbitals when ℓ is 2, and so forth. The m_ℓ quantum number has no effect on the energy of an electron unless the electrons are subjected to a magnetic field—hence its name.

The ℓ quantum number dictates the general shape of electron distribution in space (Figure **2.6.4** - Electron Orbitals). Any s orbital is spherically symmetric (Figure **2.6.4*a*** - Electron Orbitals), and there is only one orbital in any s subshell. Any p orbital has a two-lobed, dumbbell-like shape (Figure **2.6.4*b*** - Electron Orbitals); because there are three of them, we normally represent them as pointing along the x-, y-, and z-axes of Cartesian space. The d orbitals are four-lobed rosettes (Figure **2.6.4*c*** - Electron Orbitals) and they are oriented differently in space (the one labeled Math input error has two lobes and a torus instead of four lobes, but it is equivalent to the other orbitals). When there is more than one possible value of m_ℓ, each orbital is labeled with one of the possible values. It should be noted that the diagrams in Figure **2.6.4** are estimates of the electron distribution in space, not surfaces electrons are fixed on.

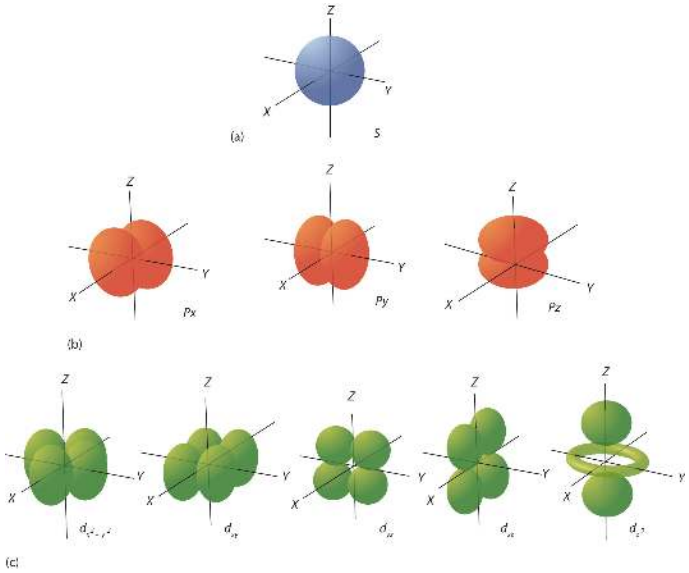


Figure **2.6.4**: Electron Orbitals. (a) The lone s orbital is spherical in distribution. (b) The three p orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five d orbitals are rosette in shape, except for the dz2 orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

The final quantum number is the **spin quantum number** (m_S). Electrons and other subatomic particles behave as if they are spinning (we cannot tell if they really are, but they behave as if they are). Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +1/2 and −1/2. These are the only two possible choices for the spin quantum number of an electron.

✔ Example 2.6.1

Of the set of quantum numbers $\{n, \ell, m\ell, m_S\}$, which are possible and which are not allowed?

a. {3, 2, 1, +1/2}
b. {2, 2, 0, −1/2}
c. {3, −1, 0, +1/2}

Solution

a. The principal quantum number n must be an integer, as it is here. The quantum number ℓ must be less than n, which it is. The $m\ell$ quantum number must be between $-\ell$ and ℓ, which it is. The spin quantum number is +1/2, which is allowed. Because this set of quantum numbers follows all restrictions, it is possible.
b. The quantum number n is an integer, but the quantum number ℓ must be less than n, which it is not. Thus, this is not an allowed set of quantum numbers.
c. The principal quantum number n is an integer, but ℓ is not allowed to be negative. Therefore, this is not an allowed set of quantum numbers.

? Exercise 2.6.1

Of the set of quantum numbers $\{n, \ell, m\ell, m_S\}$, which are possible and which are not allowed?

a. {4, 2, −2, 1}
b. {3, 1, 0, −1/2}

Answers

a. Spin must be either +1/2 or −1/2, so this set of quantum number is not allowed.
b. allowed

Chemistry is Everywhere: Neon Lights

A neon light is basically an electrified tube with a small amount of gas in it. Electricity excites electrons in the gas atoms, which then give off light as the electrons go back into a lower energy state. However, many so-called "neon" lights do not contain neon!

Although we know now that a gas discharge gives off only certain colors of light, without a prism or other component to separate the individual light colors, we see a composite of all the colors emitted. It is not unusual for a certain color to predominate. True neon lights, with neon gas in them, have a reddish-orange light due to the large amount of red-, orange-, and yellow-colored light emitted. However, if krypton is used instead of neon, a whitish light is emitted, while using argon yields a blue-purple light. A light filled with nitrogen gas glows purple, as does a helium lamp. Other gases—and mixtures of gases—emit other colors of light. Ironically, despite its importance in the development of modern electronic theory, hydrogen lamps emit little visible light and are rarely used for illumination purposes.



The Human/Need/Desire statue consists of purple "NEED", orange "HUMAN", green "HUMAN", pink "DESIRE", red "HOPE", and blue "DREAM".

Neon lights. The different colors of these "neon" lights are caused by gases other than neon in the discharge tubes. Human/Need/Desire. Neon sculpture by Bruce Nauman (1983), who has been characterized as a conceptual artist. (CC BY-SA 3.0; eschipul).

Key Takeaways

Electrons in atoms have quantized energies. The state of electrons in atoms is described by four quantum numbers.

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2.7: Organization of Electrons in Atoms

Learning Objectives

- Learn how electrons are organized within atoms.
- Represent the organization of electrons by an electron configuration.

Now that you know that electrons have quantum numbers, how are they arranged in atoms? The key to understanding electronic arrangement is summarized in the **Pauli exclusion principle:** no two electrons in an atom can have the same set of four quantum numbers. This dramatically limits the number of electrons that can exist in a shell or a subshell.

Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies. Consider H, an atom with a single electron only. Under normal conditions, the single electron would go into the n = 1 shell, which has only a single s subshell with one orbital (because m_ℓ can equal only 0). The convention is to label the shell-subshell combination with the number of the shell and the letter that represents the subshell. Thus, the electron goes in the 1s shell-subshell combination. It is usually not necessary to specify the m_ℓ or m_s quantum numbers, but for the H atom, the electron has $m_\ell = 0$ (the only possible value) and an m_s of either +1/2 or −1/2.

The He atom has two electrons. The second electron can also go into the 1s shell-subshell combination, but only if its spin quantum number is different from the first electron's spin quantum number. Thus, the sets of quantum numbers for the two electrons are {1, 0, 0, +1/2} and {1, 0, 0, −1/2}. Notice that the overall set is different for the two electrons, as required by the Pauli exclusion principle.

The next atom is Li, with three electrons. However, now the Pauli exclusion principle implies that we cannot put that electron in the 1s shell-subshell because no matter how we try, this third electron would have the same set of four quantum numbers as one of the first two electrons. So this third electron must be assigned to a different shell-subshell combination. However, the n = 1 shell doesn't have another subshell; it is restricted to having just $\ell = 0$, or an s subshell. Therefore, this third electron has to be assigned to the n = 2 shell, which has an s ($\ell = 0$) subshell and a p ($\ell = 1$) subshell. Again, we usually start with the lowest quantum number, so this third electron is assigned to the 2s shell-subshell combination of quantum numbers.

The Pauli exclusion principle has the net effect of limiting the number of electrons that can be assigned a shell-subshell combination of quantum numbers. For example, in any s subshell, no matter what the shell number, there can be a maximum of only two electrons. Once the s subshell is filled up, any additional electrons must go to another subshell in the shell (if it exists), or to a higher-numbered shell. A similar analysis shows that a p subshell can hold a maximum of six electrons. A d subshell can hold a maximum of 10 electrons, while an f subshell can have a maximum of 14 electrons. By limiting subshells to these maxima, we can distribute the available electrons to their shells and subshells.

Example 2.7.1: Carbon Atoms

How would the six electrons for C be assigned to the n and ℓ quantum numbers?

Solution

The first two electrons go into the 1s shell-subshell combination. Two additional electrons can go into the 2s shell-subshell, but now this subshell is filled with the maximum number of electrons. The n = 2 shell also has a p subshell, so the remaining two electrons can go into the 2p subshell. The 2p subshell is not completely full because it can hold a maximum of six electrons.

Exercise 2.7.1: Sodium Atoms

How would the 11 electrons for Na be assigned to the n and ℓ quantum numbers?

Answer

two 1s electrons, two 2s electrons, six 2p electrons, and one 3s electron

Now that we see how electrons are partitioned among the shells and subshells, we need a more concise way of communicating this partitioning. Chemists use an **electron configuration** to represent the organization of electrons in shells and subshells in an atom. An electron configuration simply lists 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.

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

$$\text{H: } 1s^1$$

The He atom has two electrons in the 1s subshell. Its electron configuration is

$$\text{He: } 1s^2$$

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

$$\text{Li: } 1s^2 2s^1$$

The Be atom has four electrons, two in the 1s subshell and two in the 2s subshell. Its electron configuration is

$$\text{Be: } 1s^2 2s^2$$

Now that the 2s subshell is filled, electrons in larger atoms must go into the 2p subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

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

Now that the 2p subshell is filled (all possible subshells in the n = 2 shell), the next electron for the next-larger atom must go into the n = 3 shell, s subshell.

Example 2.7.2: Sodium

What is the electron configuration for Na, which has 11 electrons?

Solution

The first two electrons occupy the 1s subshell. The next two occupy the 2s subshell, while the next six electrons occupy the 2p subshell. This gives us 10 electrons so far, with 1 electron left. This last electron goes into the n = 3 shell, s subshell. Thus, the electron configuration of Na is $1s^2 2s^2 2p^6 3s^1$.

Exercise 2.7.2: Magnesium

What is the electron configuration for Mg, which has 12 electrons?

Answer

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

For larger atoms, the electron arrangement becomes more complicated. This is because after the 3p subshell is filled, filling the 4s subshell first actually leads to a lesser overall energy than filling the 3d subshell. Recall that while the principal quantum number largely dictates the energy of an electron, the angular momentum quantum number also has an impact on energy; by the time we get to the 3d and 4s subshells, we see overlap in the filling of the shells. Thus, after the 3p subshell is completely filled (which occurs for Ar), the next electron for K occupies the 4s subshell, not the 3d subshell:

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1,$$

not

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$$

For larger and larger atoms, the order of filling the shells and subshells seems to become even more complicated. There are some useful ways to remember the order, like that shown in Figure **2.7.1**. If you follow the arrows in order, they pass through the subshells in the order that they are filled with electrons in larger atoms. Initially, the order is the same as the expected shell-subshell order, but for larger atoms, there is some shifting around of the principal quantum numbers. However, Figure **2.7.1** gives a valid ordering of filling subshells with electrons for most atoms.

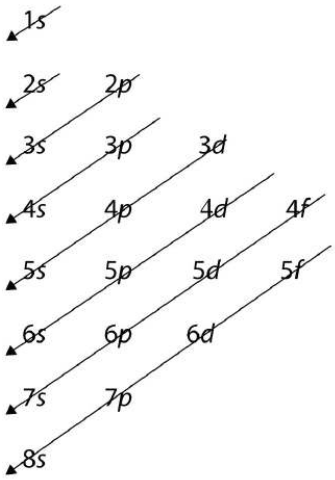


Figure **2.7.1** Electron Shell Filling Order. Starting with the top arrow, follow each arrow. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms. The n = 5 and higher shells have more subshells, but only those subshells that are needed to accommodate the electrons of the known elements are given.

The electron shell filling order goes as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, then 8s.

✔ Example **2.7.3**: Tin

What is the predicted electron configuration for Sn, which has 50 electrons?

Solution

We will follow the chart in Figure 8.4., until we can accommodate 50 electrons in the subshells in the proper order: Sn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$

Verify by adding the superscripts, which indicate the number of electrons: 2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 2 = 50, so we have placed all 50 electrons in subshells in the proper order.

? Exercise **2.7.3**: Barium

What is the electron configuration for Ba, which has 56 electrons?

Answer

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$

As the previous example demonstrated, electron configurations can get fairly long. An **abbreviated electron configuration** uses one of the elements from the last column of the periodic table, which contains the noble gases, to represent the core of electrons up to that element. Then, the remaining electrons are listed explicitly. For example, the abbreviated electron configuration for Li, which has three electrons, would be

$$\text{Li: [He]}2s^1$$

where [He] represents the two-electron core that is equivalent to He's electron configuration. The square brackets represent the electron configuration of a noble gas. This is not much of an abbreviation. However, consider the abbreviated electron configuration for W, which has 74 electrons:

$$\text{W: [Xe]}6s^2 4f^{14} 5d^4$$

This is a significant simplification over an explicit listing of all 74 electrons. So for larger elements, the abbreviated electron configuration can be a very useful shorthand.

Example 2.7.4: Phosphorus

What is the abbreviated electron configuration for P, which has 15 electrons?

Solution

With 15 electrons, the electron configuration of P is

$$\text{P: } 1s^2 2s^2 2p^6 3s^2 3p^3$$

The first immediate noble gas is Ne, which has an electron configuration of $1s^2 2s^2 2p^6$. Using the electron configuration of Ne to represent the first 10 electrons, the abbreviated electron configuration of P is

$$\text{P: [Ne]}3s^2 3p^3$$

Exercise 2.7.4: Rubidium

What is the abbreviated electron configuration for Rb, which has 37 electrons?

Answer

$\text{[Kr]}5s^1$

There are some exceptions to the rigorous filling of subshells by electrons. In many cases, an electron goes from a higher-numbered shell to a lower-numbered, but later-filled, subshell to fill the later-filled subshell. One example is Ag. With 47 electrons, its electron configuration is predicted to be

$$\text{Ag: [Kr]}5s^2 4d^9$$

However, experiments have shown that the electron configuration is actually

$$\text{Ag: [Kr]}5s^1 4d^{10}$$

This, then, qualifies as an exception to our expectations. At this point, you do not need to memorize the exceptions; but if you come across one, understand that it is an exception to the normal rules of filling subshells with electrons, which can happen.

Summary

The Pauli exclusion principle limits the number of electrons in the subshells and shells. Electrons in larger atoms fill shells and subshells in a regular pattern that can be followed. Electron configurations are a shorthand method of indicating what subshells electrons occupy in atoms. Abbreviated electron configurations are a simpler way of representing electron configurations for larger atoms. Exceptions to the strict filling of subshells with electrons do occur.

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2.7.1: Atomic Models of the Twentieth Century

Learning Objectives

- Compare different theories regarding electron arrangement within the atom.
- Understand the concept of quantized energy.
- Draw modified Bohr models for every element up through atomic number 20.
- Identify the valence electrons in a Bohr model.
- Realize the Roman numeral group numbers on the periodic table represent valence electrons.

Plum Pudding and Bohr Models

In the early twentieth century, scientists attempted to construct plausible models of the atom. One of first theories was proposed by J.J. Thomson, the physicist who discovered the electron. Thomson believed that the atom contained both positive and negative charges. He was not aware of the existence of a third neutrally charged particle (neutron). Using a plum pudding (today's comparison could be chocolate chip cookie dough) dessert for a visual representation, Thomson stated that the positive mass could be represented by the actual pudding component of the dessert. The negative species inside each atom would be scattered randomly like the plums in pudding (or chocolate chips in cookie dough).

Figure **2.7.1.1**: Plum pudding **Figure 2.7.1.2:** Thomson's depiction of a plum pudding atom.

By 1911, Ernest Rutherford discovered a centrally located positive core of the atom. Rutherford's nucleus would house the positive protons while the negative electrons would remain outside this core. Chemists and physicists immediately abandoned the plum pudding model and looked to describe electron placement in more detail. In 1915, the Danish physicist Niels Bohr proposed a new model of the atom that involved electrons orbiting the nucleus. Stationary states or energy levels would be fixed distances from the nucleus (see below). In this model, these energy levels or shells would be represented by the letter "n."

Figure **2.7.1.3**: The Bohr model of the atom illustrating levels of electrons.

This planetary model of the atom was attractive to scientists because it was similar to something with which they were already familiar, namely the solar system. Unfortunately, there was a serious flaw in the planetary model. It was already known that when a charged particle (such as an electron) moves in a curved path, it gives off some form of light and loses energy in doing so. This is, after all, how we produce TV signals. If the electron circling the nucleus in an atom loses energy, it would necessarily have to move closer to the nucleus as it loses energy and would eventually crash into the nucleus. These difficulties cast a shadow on the planetary model and indicated that, eventually, it would have to be replaced.



Figure **2.7.1.4**: Scientists who attended the 1927 Fifth Solvay International Conference on Electrons and Photons. Niels Bohr is seated in the second row on the far right. Image taken from: https://www.flickr.com/photos/iharsten/8710094055

Energy Levels

Bohr's electrons reside in energy levels or shells. These levels are denoted with the letter "n" and are associated with a precise energy value (units would be in Joules). Shells (or levels) closer to the nucleus would require smaller amounts of energy for an electron while orbits farther from the nucleus would require the electrons to have a greater amount of energy.

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. To imagine this phenomenon, note the ladder in the image below. Ladders contain rungs that are spaced at specified distances from the ground. On the ladder, an individual must remain on one of the rungs. He or she cannot step between the rungs and remain on the ladder successfully. The lowest rung required the least amount of energy for a person to exert. Moving to higher levels on the ladder would involve inputting more energy or effort.

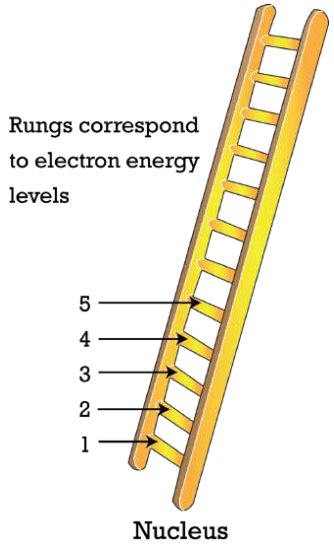


Figure **2.7.1.5**: The concept of energy levels can be view within the context of a ladder. Each allowed electronic state has an energy. For an atom, the rungs are not equally spaced.

In the Bohr atom, the rungs represent energy levels. Electrons remain in these levels until they absorb or emit a quantum of energy. When an electron gains energy, then it will move further away from the nucleus to a higher energy level. Upon emission of energy (see the red arrow in the image below), the electron will fall back to a lower energy level. The energy absorbed or emitted during these transitions is quantized.

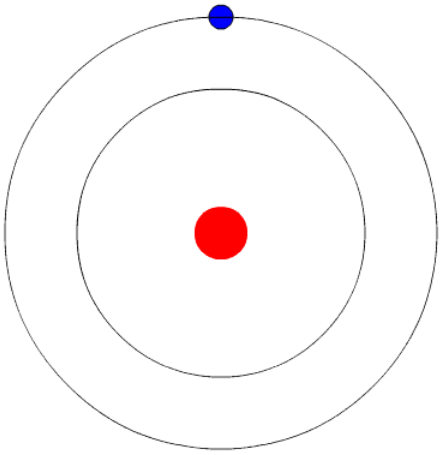


Figure **2.7.1.6**: In Bohr's Model of the atom, electrons absorb energy to move to a higher level and release energy to move to lower levels. (CC BY-SA 3.0; Kurzon).

Drawing Bohr Models

Although not completely correct, the Bohr model can give us a visual representation of electronic levels in atoms. Bohr used the formula $2n^2$ to calculate maximum number of electrons that could be housed in an energy level or shell. In this formula, "n" represents the particular energy level. When substituting an integer above the number zero, one can obtain maximum electrons for each shell. For example, the first energy level would be n =1 and this level could hold $2(1)^2 = 2$ maximum electrons. The second energy level could accommodate $2(2)^2 = 8$ electrons. In drawing Bohr diagrams, different amounts of shells are required to store a specific atom's electrons. Looking at a Bohr diagram for the carbon atom, one can see that two energy levels/shells are required for its six electrons.

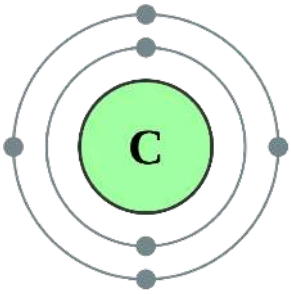


Figure **2.7.1.7**: Electron shell diagram for carbon, the 6th element in the periodic table of elements. (CC BY-SA 2.0(UK); Pumbaa)

Bohr diagrams for a variety of elements are illustrated in chart below **.** When determining the number of electrons of an atom, remember to refer to the atomic number (the whole number) on the periodic table.

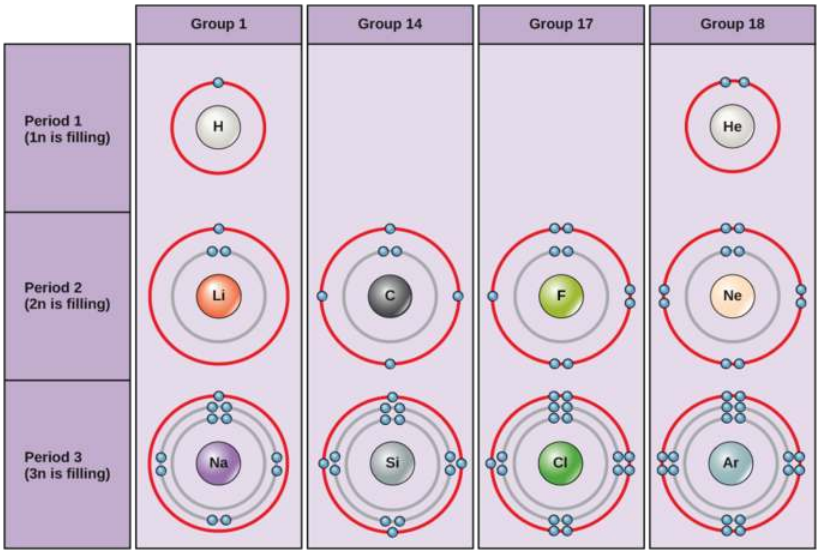


Figure **2.7.1.8**: Bohr models of different groups/families of elements from the periodic table.

In this course, we will be using a **modified Bohr model**. In other words, we will limit each shell after n=1 to a maximum of eight total electrons. We will also be limited in drawing Bohr diagrams of only the first twenty elements on the periodic table. This process will allow us to identify the **valence** or active electrons of these particular elements. Watch this video of your professor drawing Bohr models and identifying valence electrons.

✔ Example 2.7.1.1: Drawing BOhr Diagrams

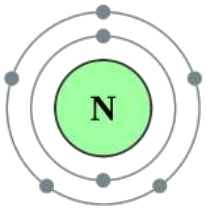
Draw modified Bohr diagrams for

a. nitrogen
b. calcium
c. sulfur

Feb 18, 2018, 6:12 PM

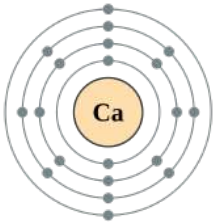
commons.wikimedia.org/wiki/E...-_no_label.svg

Answer a



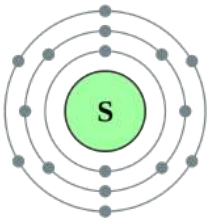
Bohr model of nitrogen: (CC BY-SA 2.0 uk; *Greg Robson):*

Answer b



Bohr model of calcium: (CC BY-SA 2.0 uk;*Greg Robson):*

Answer b



Bohr model of sulfur: (CC BY-SA 2.0 uk; Greg Robson).

Valence electrons are located in the highest energy level of an atom. When drawing a Bohr diagram, the valence electrons would be present in the outermost electronic level/shell (furthest away from the nucleus). An atom can have from one to eight valence electrons. In the bonding process, atoms will either gain, lose, or share valence electrons to become more stable. A quick method of checking valence electrons is to refer to an element's group number (in Roman numerals) on the periodic table. Even if you cannot draw a Bohr diagram (Bohr's are limited to elements with atomic numbers (Z)< 21), you can still determine valence electrons by looking to the group number.

Example 2.7.1.2: Identifying Valence Electrons

From the Bohr Diagrams constructed in Example **2.7.1.1**, how many valence electrons are on each atom.

Answer a

Five.

Answer b

Two

Answer c

Six

Quantum Theory

The Bohr Theory failed to explain why the electron did not spiral into the nucleus after a certain amount of revolutions around the nucleus. In addition, this theory had difficulty diagramming multi-electron systems (atoms or ions with more than one electron). For these reasons, scientists turned to the quantum mechanical theory. Since 1927, this has been the working theory that most chemistry courses use (we will not use this theory in our course). For a more detailed explanation of quantum mechanics, click here.

Summary

- The Bohr model postulates that electrons orbit the nucleus at fixed energy levels.
- Orbits further from the nucleus exist at higher energy levels.
- When electrons return to a lower energy level, they emit energy in the form of light.
- 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..

Vocabulary

- Energy levels: Possible orbits that an electron can have in the electron cloud of an atom.
- Quantized: requiring or possessing specific amounts of energy.

Contributors and Attributions

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2.8: Electronic Structure and the Periodic Table

Learning Objectives

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

In Chapter 3, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure **2.8.1**. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Figure **2.8.1**: The Periodic Table

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations, the shape of the periodic table mimics the filling of the subshells with electrons.

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

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure **2.8.2**)

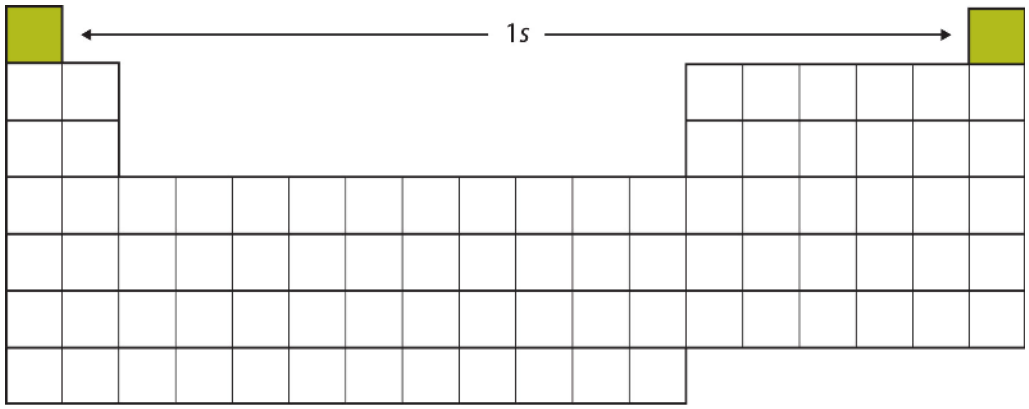


Figure 2.8.2: The 1s Subshell. H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 2.8.3 shows that these two elements are adjacent on the periodic table.

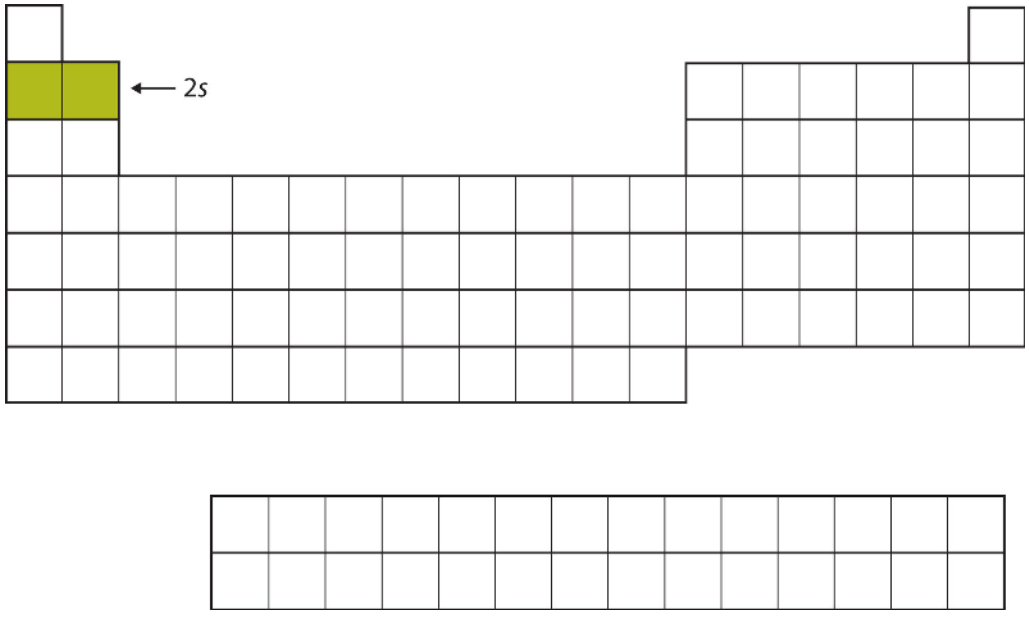


Figure 2.8.3: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 2.8.4).

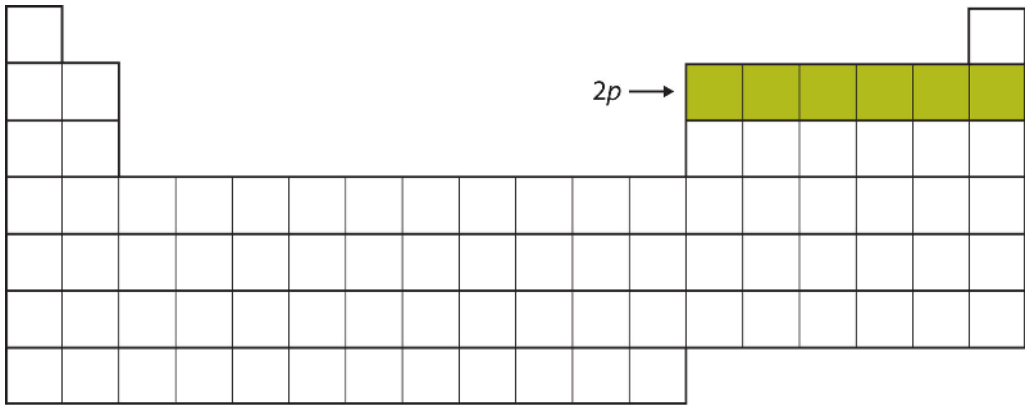


Figure 2.8.4: The 2p Subshell. For B through Ne, the 2p subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements coinciding this subshell being filled, Na and Mg, are back on the left side of the periodic table (Figure 2.8.5).

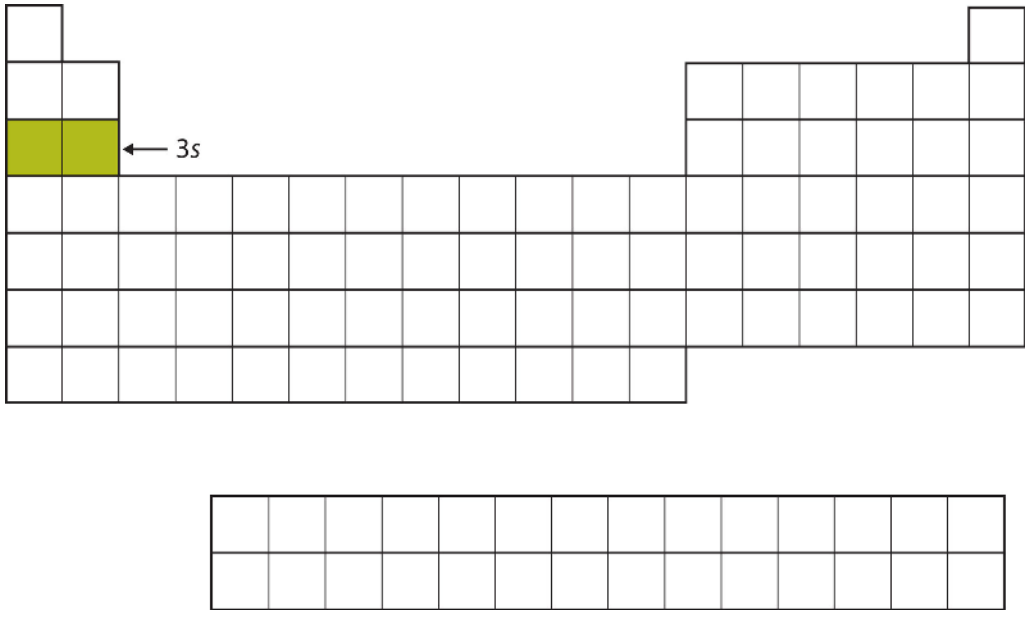


Figure 2.8.5: The 3s Subshell. Now the 3s subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 2.8.6).

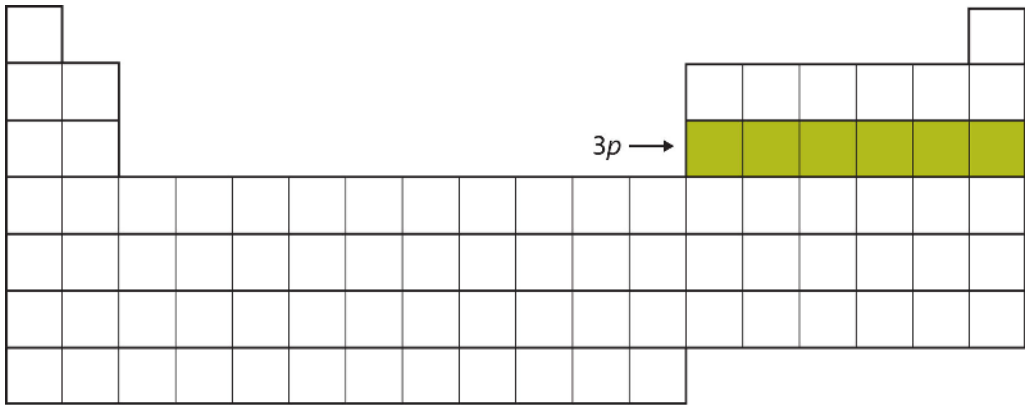


Figure8.5.6: The 3p Subshell. Next, the 3p subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure **2.8.7**).

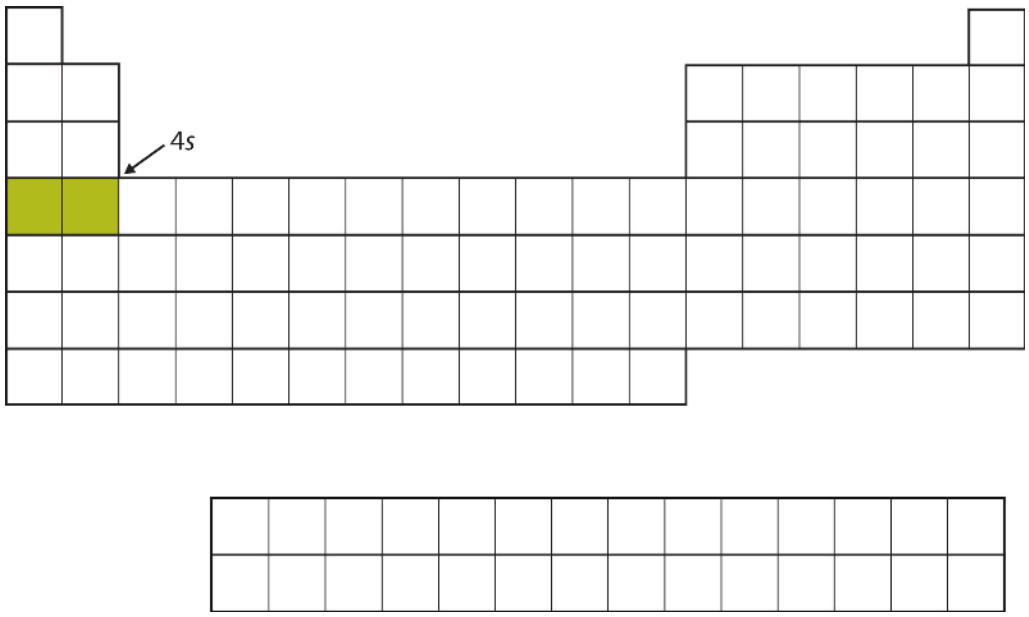


Figure **2.8.7**: The 4s Subshell. The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure **2.8.8**).

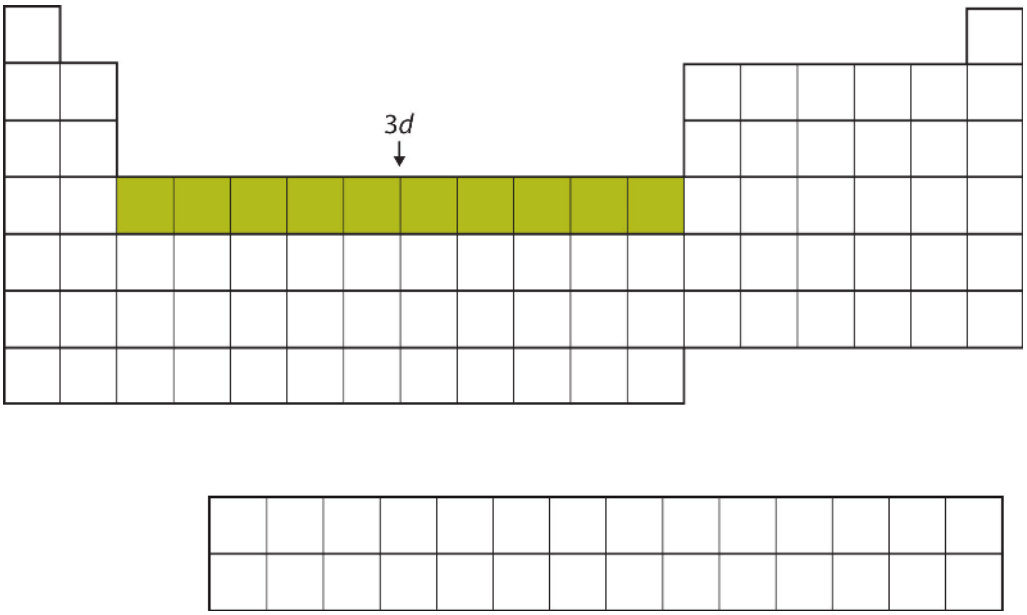


Figure 2.8.8: The 3d Subshell. The 3d subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** is the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 2.8.9 shows the blocks of the periodic table.

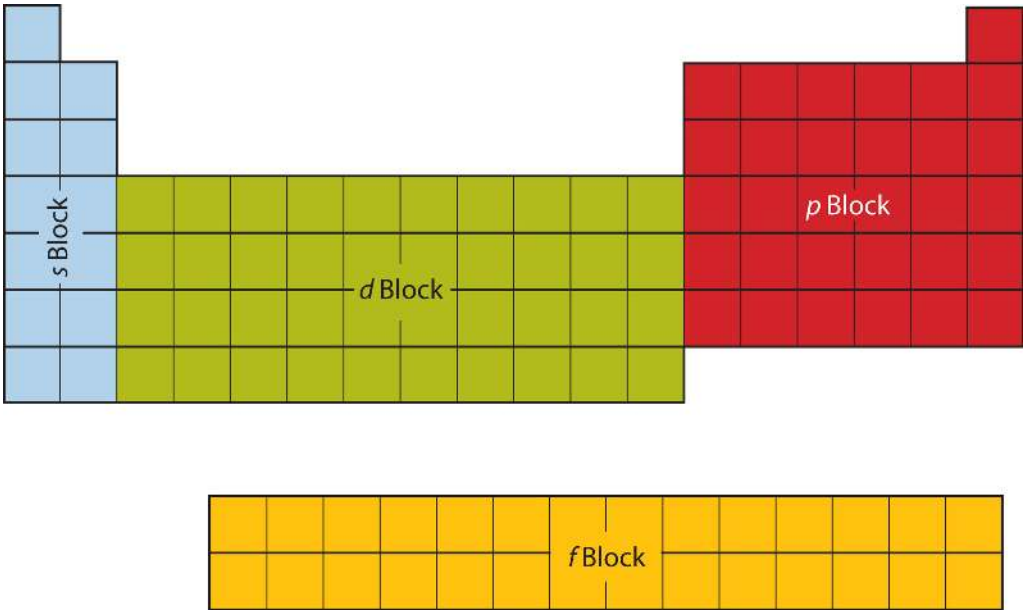


Figure 2.8.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

Empty periodic table, separated into 4 different colored blocks. S block is blue, d block is green, p block is red and f block is orange.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the

valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Table with two columns and 6 rows. The first column on the left has various elements in the rows underneath. The second column on the right has the different corresponding electron configurations for the specified element in the rows underneath.

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

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

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

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure **2.8.10**. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

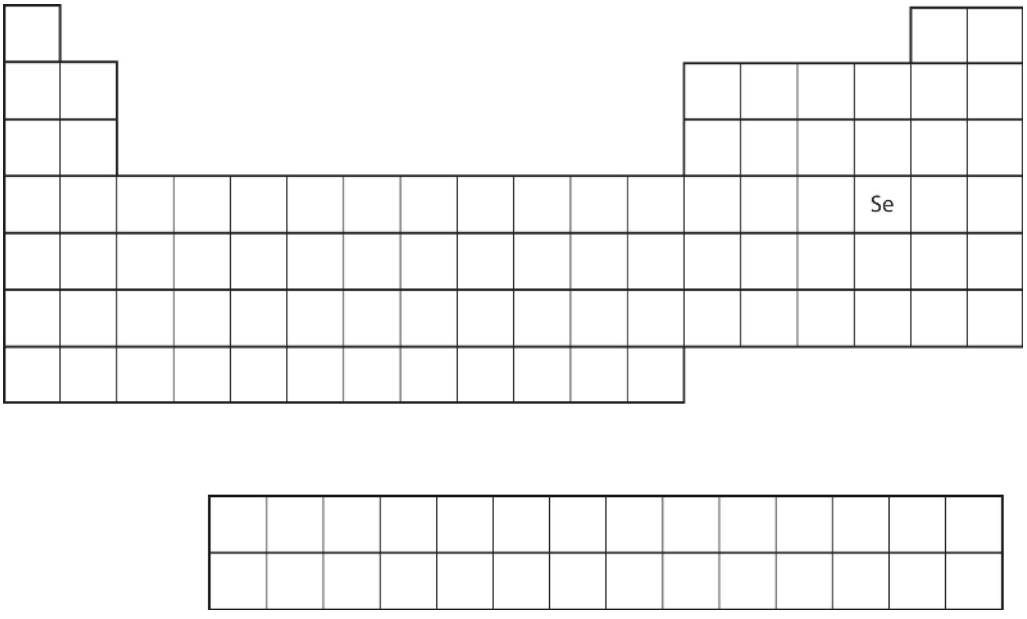


Figure **2.8.10**: Selenium on the Periodic Table

Example 2.8.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure **2.8.11**).

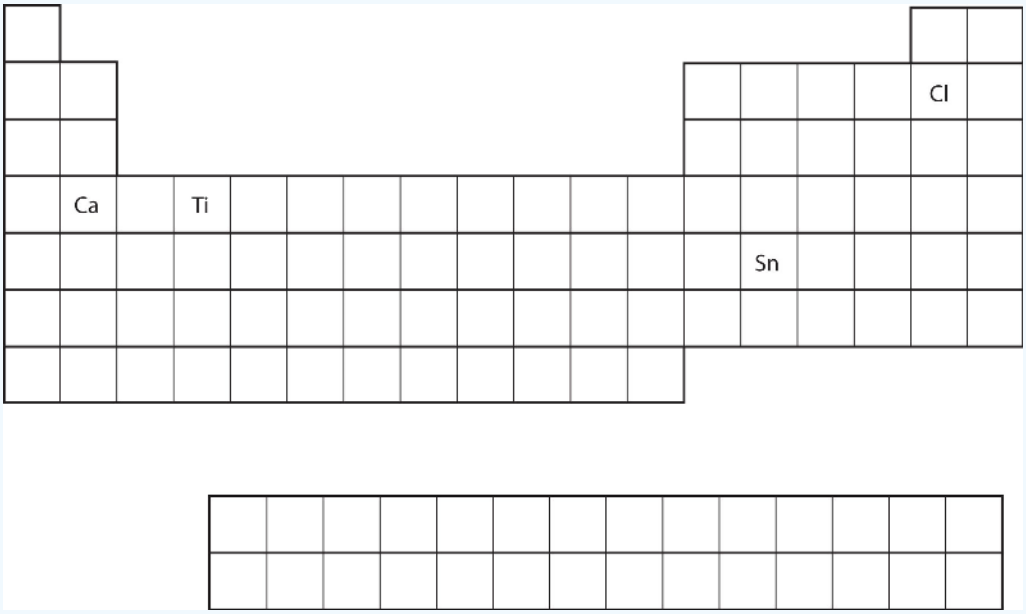


Figure **2.8.11**: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is $[Ar]4s^2$.
2. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is $[Kr]5s^24d^{10}5p^2$.

Exercise 2.8.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure **2.8.11**.

a. Ti
b. Cl

Answer a

$[Ar]4s^23d^2$

Answer b

$[Ne]3s^23p^5$

Food and Drink Application: Artificial Colors

The color of objects comes from a different mechanism than the colors of neon and other discharge lights. Although colored lights produce their colors, objects are colored because they preferentially reflect a certain color from the white light that shines on them. A red tomato, for example, is bright red because it reflects red light while absorbing all the other colors of the rainbow.

Many foods, such as tomatoes, are highly colored; in fact, the common statement "you eat with your eyes first" is an implicit recognition that the visual appeal of food is just as important as its taste. But what about processed foods?

Many processed foods have food colorings added to them. There are two types of food colorings: natural and artificial. Natural food colorings include caramelized sugar for brown; annatto, turmeric, and saffron for various shades of orange or yellow; betanin from beets for purple; and even carmine, a deep red dye that is extracted from the cochineal, a small insect that is a parasite on cacti in Central and South America. (That's right—you may be eating bug juice!)

Some colorings are artificial. In the United States, the Food and Drug Administration currently approves only seven compounds as artificial colorings in food, beverages, and cosmetics:

- FD&C Blue #1: Brilliant Blue FCF
- FD&C Blue #2: Indigotine
- FD&C Green #3: Fast Green FCF
- RD&C Red #3: Erythrosine
- FD&C Red #40: Allura Red AC
- FD&C Yellow #5: Tartrazine
- FD&C Yellow #6: Sunset Yellow FCF

Lower-numbered colors are no longer on the market or have been removed for various reasons. Typically, these artificial colorings are large molecules that absorb certain colors of light very strongly, making them useful even at very low concentrations in foods and cosmetics. Even at such low amounts, some critics claim that a small portion of the population (especially children) is sensitive to artificial colorings and urge that their use be curtailed or halted. However, formal studies of artificial colorings and their effects on behavior have been inconclusive or contradictory. Many people continue to enjoy processed foods with artificial coloring (like those shown in the accompanying figure).



Artificial food colorings. Artificial food colorings are found in a variety of food products, such as processed foods, candies, and egg dyes. Even pet foods have artificial food coloring in them. (CC by 2.0, Matthew Bland via Flickr.)

Summary

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

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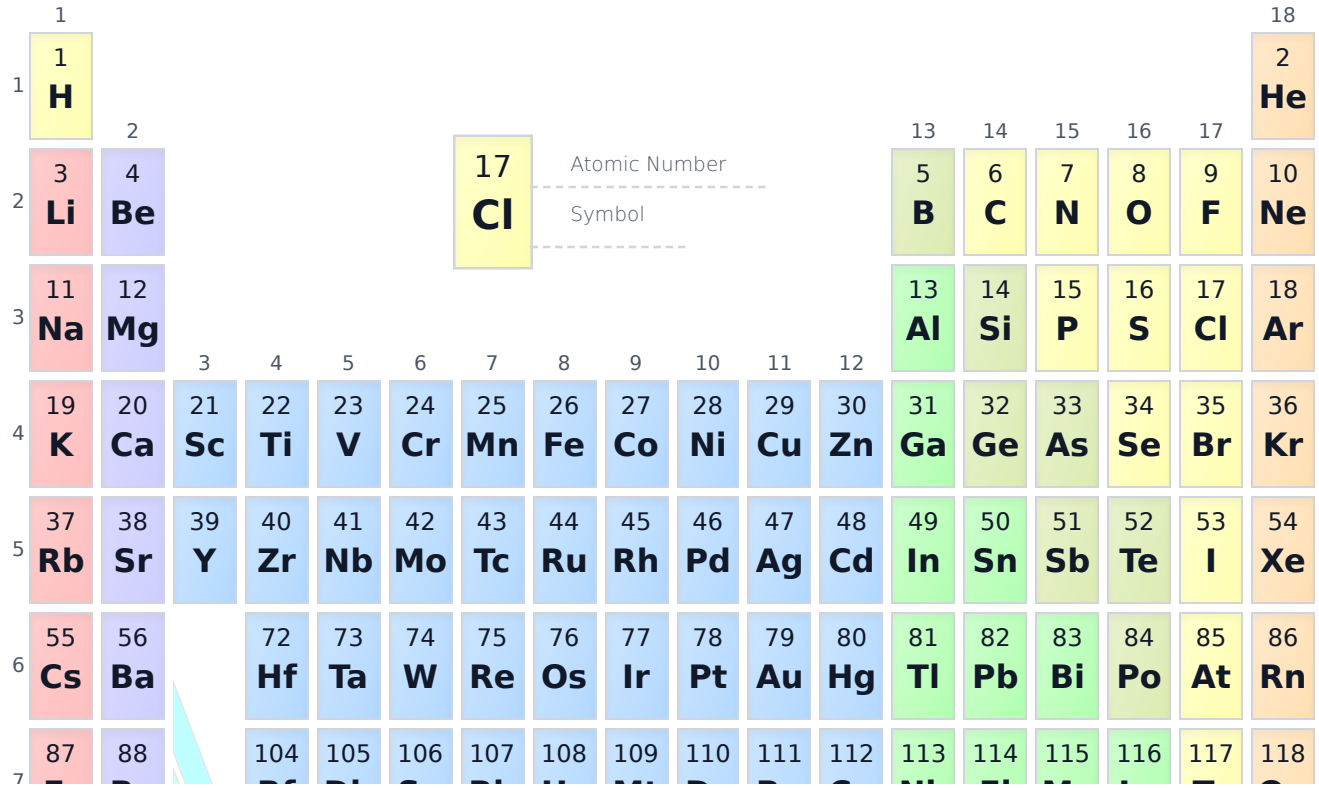
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CHAPTER OVERVIEW

3: Periodic Table of the Elements

PUBCHEM > PERIODIC TABLE

Periodic Table of Elements



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3.1.1.2: Chlorine (Chem Properties)

3.1.1.3: Group 16 (Chem Properties)

3.1.2: Environmental Properties

3.1.2.1: Chlorine (Env Properties)

3.1.3: Nuclear Properties

3.1.3.1: Chlorine (Nuke Properties)

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3.1.4.1: Beryllium (Overview)

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3.1.5.21: Phosphorus (Phys Properties)
3.1.5.22: Silicon (Phys Properties)
3.1.5.23: Sulfur (Phys Properties)

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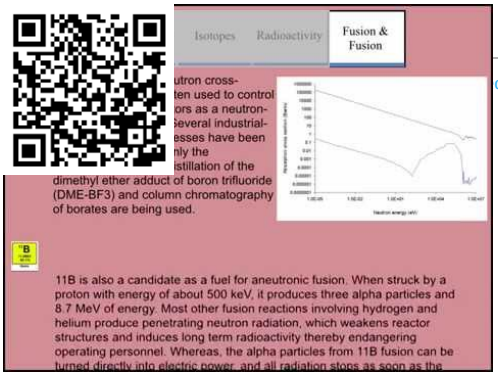
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3.1.1: Chemical Properties

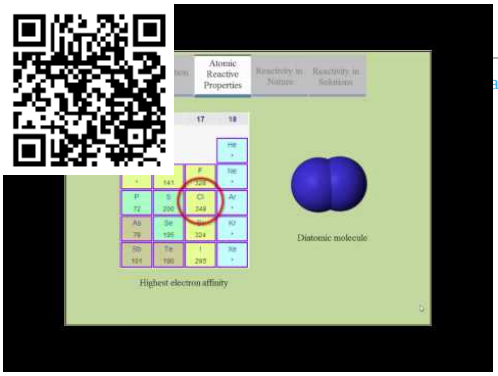
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3.1.1.1: Boron (Chem Properties)



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3.1.1.3: Group 16 (Chem Properties)



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SECTION OVERVIEW

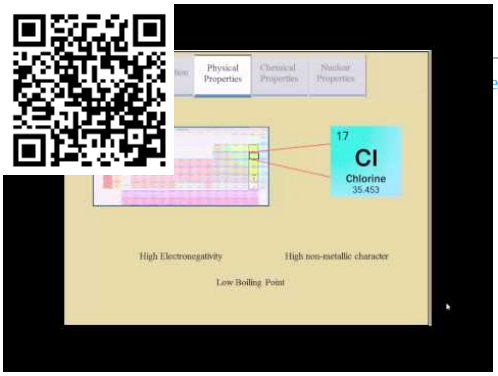
3.1.2: Environmental Properties

Topic hierarchy

3.1.2.1: Chlorine (Env Properties)

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3.1.2.1: Chlorine (Env Properties)

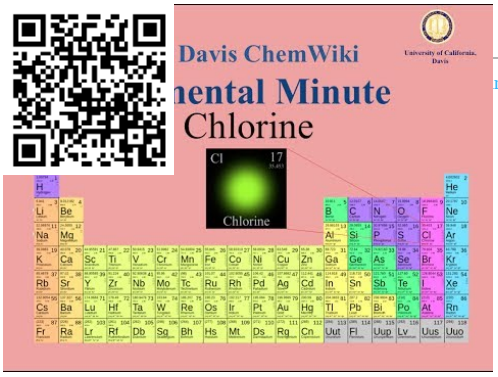


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3.1.3.1: Chlorine (Nuke Properties)

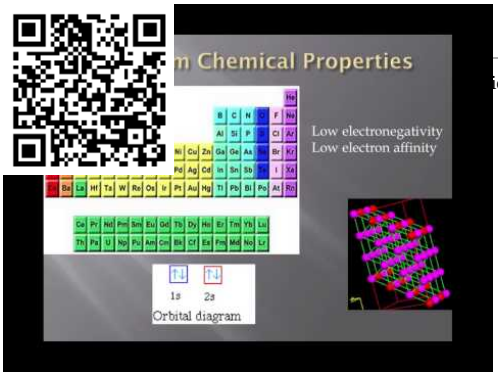


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3.1.4: Overview

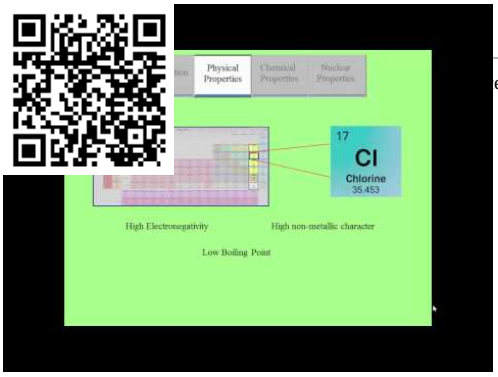
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3.1.4.1: Beryllium (Overview)



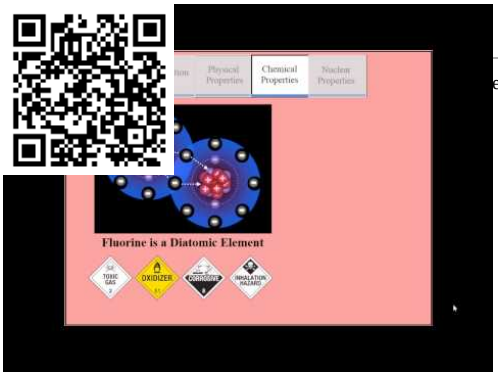
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3.1.4.2: Chlorine (Overview)



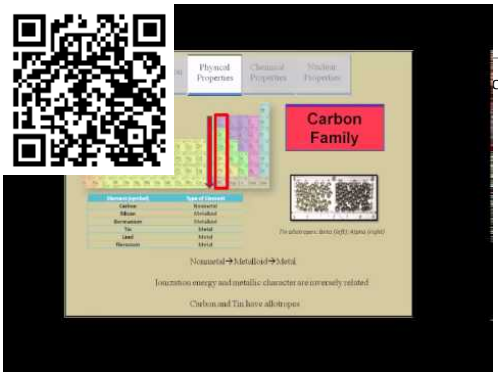
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3.1.4.3: Fluorine (Overview)



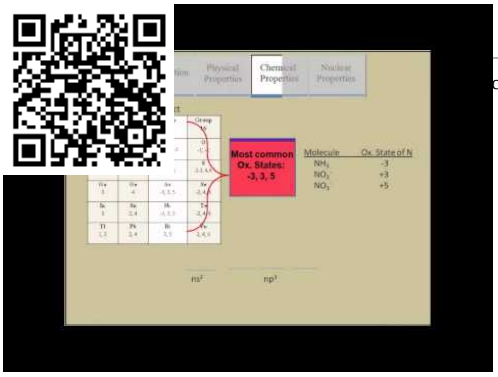
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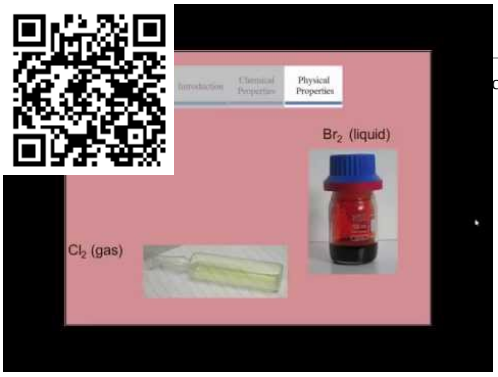
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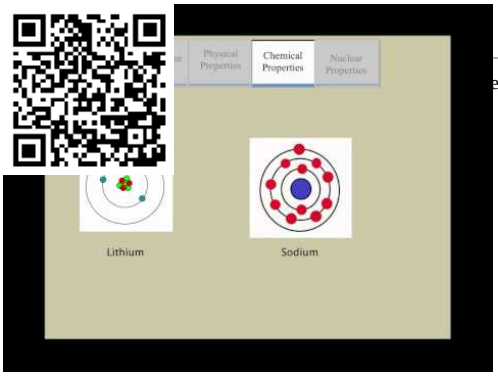
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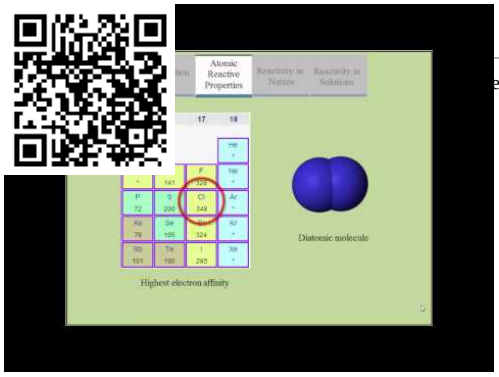
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3.1.4.7: Group 1 (Overview)



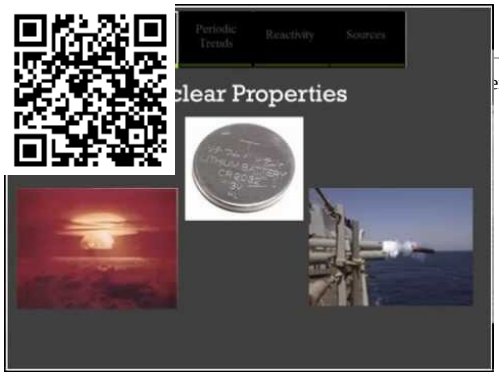
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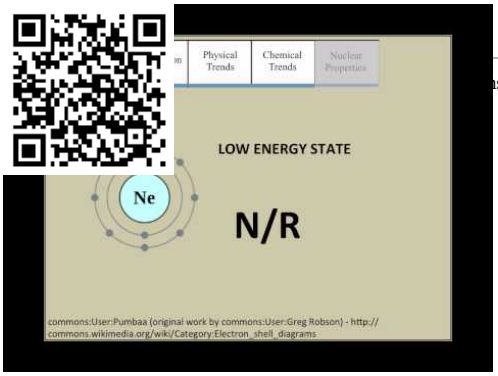
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3.1.4.9: Lithium (Overview)



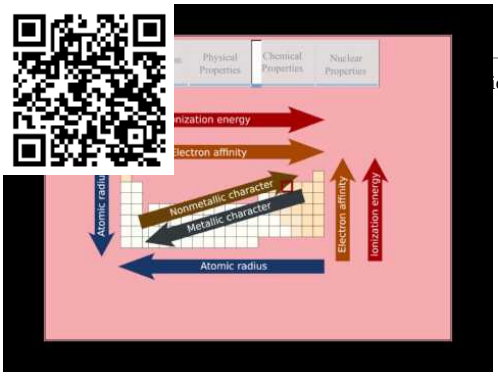
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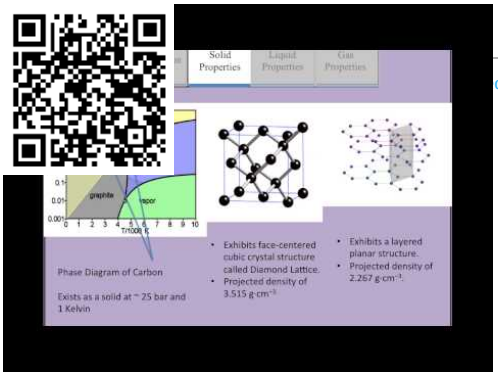
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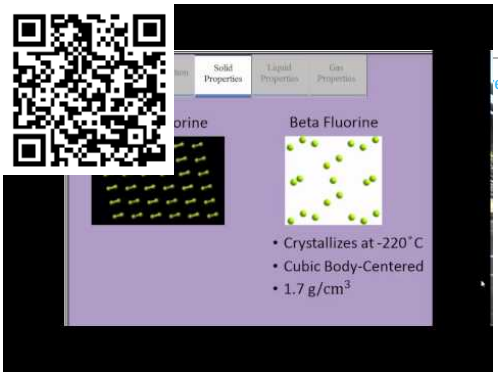


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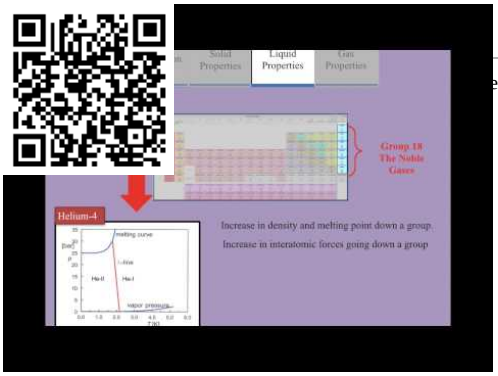
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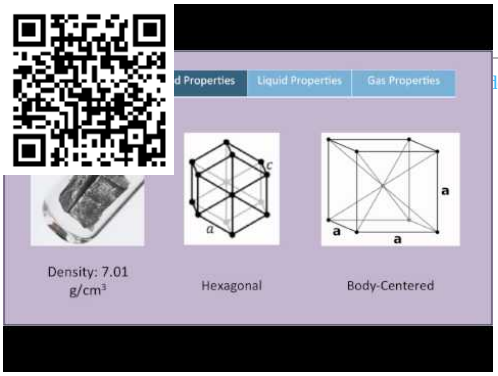
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3.1.5.12: Magnesium (Phys Properties)



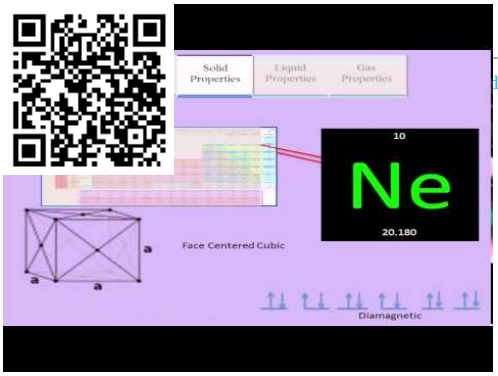
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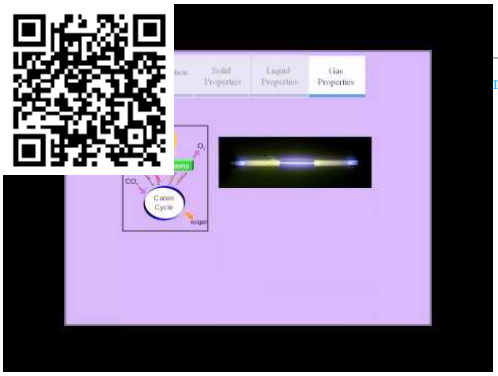


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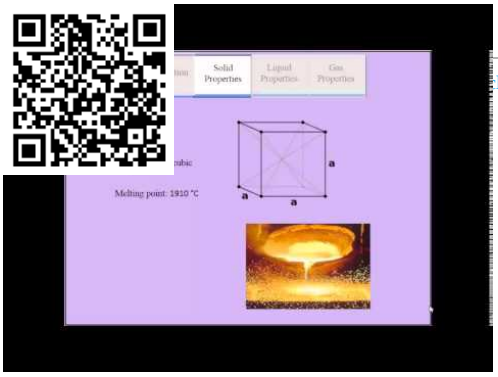
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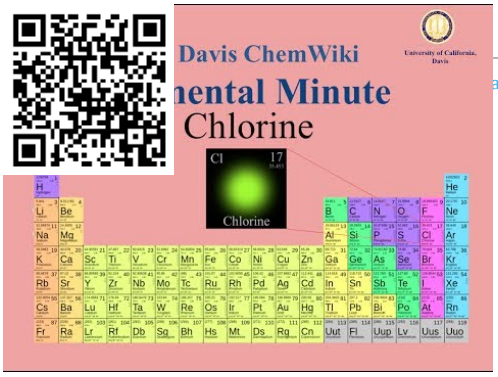
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CHAPTER OVERVIEW

4: Introduction to acids and bases

Certain household chemicals, such as some brands of cleanser, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home; if spilled on the skin, the strong caustic compound can immediately remove H+ ions from the flesh, resulting in chemical burns. Compare that to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine-all of which contain acids.

Formerly there were rather campy science-fiction television shows in which the hero was always being threatened with death by being plunged into a vat of boiling acid: "Mwa ha ha, Buck Rogers [or whatever the hero's name was], prepare to meet your doom by being dropped into a vat of boiling acid!" (The hero always escapes, of course.) This may have been interesting drama, but not very good chemistry. If the villain knew his/her/its science, the hero would have been dropped into a vat of boiling base.

Recall that the active component of a classic acid is the H^+ ion, while the active part of a classic base is the OH^- ion. Both ions are related to water in that all H^+ ion needs to become a water molecule is an OH^- ion, while all an OH^- ion needs to become water is an H^+ ion. Consider the relative masses involved: an ion of mass 1 needs an ion of mass 17 to make water, while an ion of mass 17 needs an ion of mass 1 to make water. Which process do you think will be easier?

In fact, bases are more potentially dangerous than acids because it is much easier for an OH^- ion to rip off an H^+ ion from surrounding matter than it is for an H^+ ion to rip off an OH^- ion. Certain household chemicals, such as some brands of cleaner, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home. If spilled on the skin, these strong caustic compounds can immediately remove H^+ ions from the flesh, resulting in chemical burns. Compare this to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine—all of which contain acids. (Of course, some parts of the body, such as the eyes, are extremely sensitive to acids as well as bases.) It seems that our bodies are more capable of dealing with acids than with bases.



Figure **4.1** Household chemicals © Thinkstock. On the left is a common acid, and on the right is a common base. Which one is more potentially hazardous?

A note to all of the villains out there...get your chemistry right if you want to be successful!

4.1: Brønsted-Lowry Acids and Bases
4.2: The pH Scale
4.3: pH of Chesapeake Bay

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4.1: Brønsted-Lowry Acids and Bases

Learning Objectives

- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

The Arrhenius definition of acid and base is limited to aqueous (that is, water) solutions. Although this is useful because water is a common solvent, it is limited to the relationship between the H^+ ion and the OH^- ion. What would be useful is a general definition more applicable to other chemical reactions and, importantly, independent of H_2O.

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).

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the prototypical Arrhenius acid-base reaction:

$$\underset{acid}{H^+(aq)} + \underset{base}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Acid species and base species are marked. The proton, however, is (by definition) a proton donor (labeled PD), while the OH^- ion is acting as the proton acceptor (labeled PA):

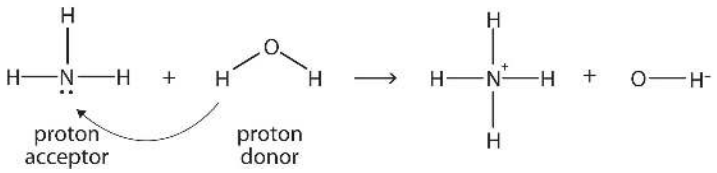
$$\underset{PD}{H^+(aq)} + \underset{PA}{OH^-(aq)} \rightarrow H_2O\,(l)$$

The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\underset{BL\ acid}{H^+(aq)} + \underset{BL\ base}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Thus H^+ is an acid by both definitions, and OH^- is a base by both definitions.

Ammonia (NH_3) is a base even though it does not contain OH^- ions in its formula. Instead, it generates OH^- ions as the product of a proton-transfer reaction with H_2O molecules; NH_3 acts like a Brønsted-Lowry base, and H_2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH_3 hydrolyzes to make NH_4^+ ions and OH^- ions.

Even the dissolving of an Arrhenius acid in water can be considered a Brønsted-Lowry acid-base reaction. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$HCl\,(g) + H_2O(\ell) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H_2O is the proton acceptor and a Brønsted-Lowry base. These two examples show that H_2O can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

Example 4.1.1

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

$$C_6H_5OH + NH_2^- \longrightarrow C_6H_5O^- + NH_3$$

Solution

The C_6H_5OH molecule is losing an H^+; it is the proton donor and the Brønsted-Lowry acid. The NH_2^- ion (called the amide ion) is accepting the H^+ ion to become NH_3, so it is the Brønsted-Lowry base.

Exercise 4.1.1: Aluminum Ions in Solution

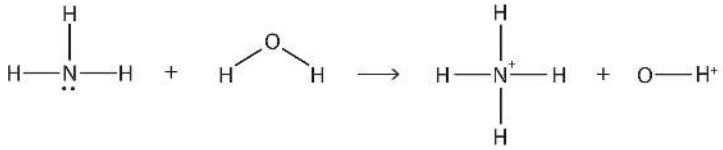
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+$$

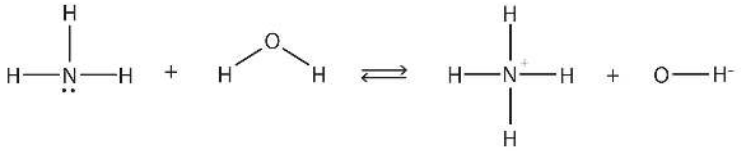
Answer

Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: H_2O

In the reaction between NH_3 and H_2O,



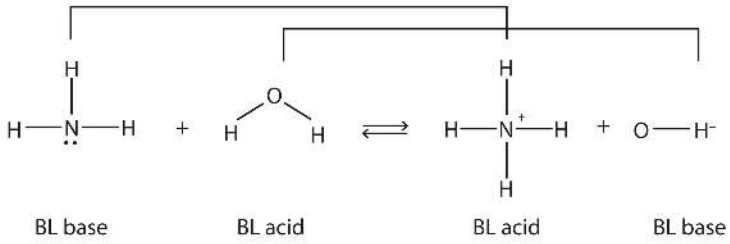
the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change of the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:



What do you notice about the reverse reaction? The NH_4^+ ion is donating a proton to the OH^- ion, which is accepting it. This means that the NH_4^+ ion is acting as the proton donor, or Brønsted-Lowry acid, while the OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:

BL bases. NH4+ and H2O are the BL acids. lt-chem-64081" style="width: 750px; height: 173px;" width="750px" height="173px" src="/@api/deki/files/92035/3765cabac9591a0fb3dd5878f56075e2.jpg" data-quail-id="174">

This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:



The two sets—NH_3/NH_4^+ and H_2O/OH^-—are called **conjugate acid-base pairs**. We say that NH_4^+ is the conjugate acid of NH_3, OH^- is the conjugate base of H_2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs.

✔ Example 4.1.2

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 4.1.2

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)

✔ Chemistry is Everywhere: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for HCl(aq). In Section 4.6, vinegar was mentioned as a dilute solution of acetic acid [$HC_2H_3O_2$(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is NH_3, which is found in numerous cleaning products. NH_3 is a base because it increases the OH^- ion concentration by reacting with H_2O:

$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H_2O and forming excess OH^- ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body tissues and other substances in our bodies. Thus when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, non-lye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.



Figure **4.1.1** Drain Cleaners. Drain cleaners can be made from a reactive material that is less caustic than a base. Source: Photo used by permission of Citrasolv, LLC.

Key Takeaways

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.

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4.2: The pH Scale

Learning Objectives

- Define *pH*.
- Determine the pH of acidic and basic solutions.

As we have seen, $[H^+]$ and $[OH^-]$ values 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.

pH is commonly defined as a logarithmic function of $[H^+]$:

$$\mathbf{pH = -\log[H^+]} \tag{4.2.1}$$

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.

This is known as the pH scale and is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to quickly determine whether a given aqueous solution is acidic, basic, or neutral.

Example 4.2.1

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

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

Exercise 4.2.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

1. human blood, pH = 7.4
2. household ammonia, pH = 11.0
3. cherries, pH = 3.6

Answers

1. basic
2. basic
3. acidic

Table 4.2.1 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 4.2.1 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	

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.

Using the definition of pH (Equation 4.2.1), it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

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

Key Takeaways

- pH is a logarithmic function of $[H^+]$.
- $[H^+]$ can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.

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4.3: pH of Chesapeake Bay

pH is measured on a scale of 1 – 14 with 7 being neutral; (see figure 1.) The lower the number the more acidic a solution is, the higher the number the more basic it is. What does acidic or basic mean? Acidity means there are more hydronium ions than hydroxide ions and vice versa for basic solutions. Why care about pH and pOH? All organisms live in certain pH and pOH levels. Your body tends to be between a pH of 7.35 and 7.45. When the pH is higher or lower than the preferred range, your body does not function well. If your body is acidic (lower than pH of 7,) you can develop problems such as inflammation and wearing away of body tissue. This can lead to cancer, heart disease, or diabetes. Your body prefers a slightly basic (higher than 7 pH) environment. But if it gets too high, it can cause digestive and respiration problems. There is a great balancing act happening. The same is happening in the Chesapeake Bay.

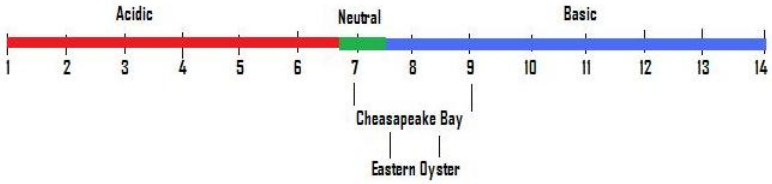


Figure 4.3.1: pH Scale

The Chesapeake tends to be between a pH of 7 and 9. When extra nutrients from farming (such as from fertilizers) leak into the water supply, algae can thrive and bloom (see Figure 2.) This causes an imbalance in the environment and creates a more alkaline (basic) pH water environment. A pH increase of 1 is more significant than it seems. pH is a log 10 scale, so a pH of 7 has a concentration of 10^{-7} hydronium ions. A pH of 8 has a concentration of 10^{-8}. This means that a pH of 8 has 10 times less [one tenth] hydronium ions as a pH of 7 and a pH of 9 has 100 times less [one hundredth] hydronium ions than a pH of 7. So, there are consequences with just a change of 1 pH unit. To figure out the pH and pOH levels from ion concentration, use the following formulas. pH = -log (H_3O^+) and pOH = -log (OH^-).



Figure 4.3.2: A*lgae Bloom* http://drwaters.org/?itemCategory=33533&siteid=300&priorId=0

The Chesapeake Bay is home to the eastern oyster and other organisms. The eastern oyster can spawn in water with pH between 7.8 and 8.2 and had difficulties in pH that is lower than 6 or higher than 10. Larvae mortality rates increased rapidly when the pH is in the 9.00 to 9.50 range. The pH also affects respiration rate and pumping rate of water. When algae blooms occur, the oyster population suffers.



Figure 4.3.3: Eastern Oyster from the Chesapeake Bay http://www.chesapeakebay.net/fieldguide/critter/eastern_oyster

Practice Questions

Directions: Figure out the pH and pOH levels and answer the following questions.

1)What is the pH if the hydronium concentration is 10^{-5}?
pH = -log (H_3O^+)
pH = -log (10^{-5})
pH = 5

2)Would the Eastern Oyster survive in this pH? Explain.
The Eastern Oyster population would not survive in a pH of 5. The Eastern oyster needs a pH of 7.8 – 8.2 to spawn and anything under a pH of 6 makes the respiration rate decrease with spawning nearly impossible. This means that the oyster population would not increase and the oysters that were there would die off slowly due to not being able to function properly in that low of a pH.

3)What would the pOH be if the hydroxide concentration is 10<su>-8</sup>?

```
pOH = -log (OH)
```

pOH = -log (10^{-8})
pOH = 8

4)If pOH = 14 – pH, what is the pH level from your answer to number 3?
pOH = 14 – pH
8 = 14 – pH
pH + 8 = 14
pH = 14 – 8
pH = 6

5)Would the Eastern Oyster survive in this pH? Explain.
It would be possible for the Eastern Oyster to survive since they have more difficulties when the pH is lower than 6. They would be stressed, but not to the point of being unable to reproduce. This is the lowest the pH could be before the population would really start to decline. This could potentially be the “tipping point” of the population.

From ChemPRIME: 14.2: pH and pOH

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Contributors and Attributions

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CHAPTER OVERVIEW

5: Solids and Liquids

5.1: Classification of Matter
5.2: Phase Transitions - Melting, Boiling, and Subliming

Liquids flow when a small force is placed on them, even if only very slowly. Solids, however, may deform under a small force, but they return to their original shape when the force is relaxed. This is how glass behaves: it goes back to its original shape (unless it breaks under the applied force). Observers also point out that telescopes with glass lenses to focus light still do so even decades after manufacture-a circumstance that would not be so if the lens were liquid and flowed.

There is an urban legend that glass is an extremely thick liquid rather than a solid, even at room temperature. Proponents claim that old windows are thicker at the bottom than at the top, suggesting that the glass flowed down over time. Unfortunately, the proponents of this idea have no credible evidence that this is true, as old windows were likely not subject to the stricter manufacturing standards that exist today. Also, when mounting a piece of glass that has an obviously variable thickness, it makes structural sense to put the thicker part at the bottom, where it will support the object better.



Figure **5.1** A woman cleaning glass © Thinkstock. Is this woman cleaning a solid or a liquid? Contrary to some claims, glass is a solid, not a very thick liquid.

Liquids flow when a small force is placed on them, even if only very slowly. Solids may deform under a small force, but they return to their original shape when the force is relaxed. This is how glass behaves: it goes back to its original shape (unless it breaks under the applied force). Observers also point out that telescopes with glass lenses to focus light still do so even decades after manufacture—a circumstance that would not be so if the lens were liquid and flowed. Thus, glass is a solid at room temperature.

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5.1: Classification of Matter

Learning Objectives

- To classify matter.

Chemists study the structures, physical properties, and chemical properties of material substances. These consist of **matter**, which is anything that occupies space and has mass. Gold and iridium are matter, as are peanuts, people, and postage stamps. Smoke, smog, and laughing gas are matter. Energy, light, and sound, however, are not matter; ideas and emotions are also not matter.

The **mass** of an object is the quantity of matter it contains. Do not confuse an object's mass with its **weight**, which is a force caused by the gravitational attraction that operates on the object. Mass is a fundamental property of an object that does not depend on its location.In physical terms, the mass of an object is directly proportional to the force required to change its speed or direction. A more detailed discussion of the differences between weight and mass and the units used to measure them is included in Essential Skills 1 (Section 1.9). Weight, on the other hand, depends on the location of an object. An astronaut whose mass is 95 kg weighs about 210 lb on Earth but only about 35 lb on the moon because the gravitational force he or she experiences on the moon is approximately one-sixth the force experienced on Earth. For practical purposes, weight and mass are often used interchangeably in laboratories. Because the force of gravity is considered to be the same everywhere on Earth's surface, 2.2 lb (a weight) equals 1.0 kg (a mass), regardless of the location of the laboratory on Earth.

Under normal conditions, there are three distinct states of matter: solids, liquids, and gases. **Solids** are relatively rigid and have fixed shapes and volumes. A rock, for example, is a solid. In contrast, **liquids** have fixed volumes but flow to assume the shape of their containers, such as a beverage in a can. **Gases**, such as air in an automobile tire, have neither fixed shapes nor fixed volumes and expand to completely fill their containers. Whereas the volume of gases strongly depends on their temperature and **pressure** (the amount of force exerted on a given area), the volumes of liquids and solids are virtually independent of temperature and pressure. Matter can often change from one physical state to another in a process called a **physical change**. For example, liquid water can be heated to form a gas called steam, or steam can be cooled to form liquid water. However, such changes of state do not affect the chemical composition of the substance.

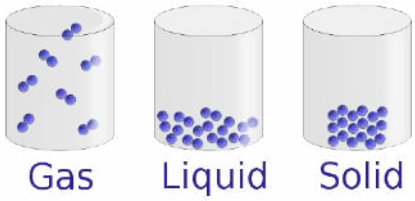


Figure **5.1.1**: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia

Pure Substances and Mixtures

A pure chemical substance is any matter that has a fixed chemical composition and characteristic properties. Oxygen, for example, is a pure chemical substance that is a colorless, odorless gas at 25°C. Very few samples of matter consist of pure substances; instead, most are mixtures, which are combinations of two or more pure substances in variable proportions in which the individual substances retain their identity. Air, tap water, milk, blue cheese, bread, and dirt are all mixtures. If all portions of a material are in the same state, have no visible boundaries, and are uniform throughout, then the material is **homogeneous**. Examples of homogeneous mixtures are the air we breathe and the tap water we drink. Homogeneous mixtures are also called solutions. Thus air is a solution of nitrogen, oxygen, water vapor, carbon dioxide, and several other gases; tap water is a solution of small amounts of several substances in water. The specific compositions of both of these solutions are not fixed, however, but depend on both source and location; for example, the composition of tap water in Boise, Idaho, is not the same as the composition of tap water in Buffalo, New York. Although most solutions we encounter are liquid, solutions can also be solid. The gray substance still used by some dentists to fill tooth cavities is a complex solid solution that contains 50% mercury and 50% of a powder that contains mostly silver, tin, and copper, with small amounts of zinc and mercury. Solid solutions of two or more metals are commonly called alloys.

If the composition of a material is not completely uniform, then it is **heterogeneous** (e.g., chocolate chip cookie dough, blue cheese, and dirt). Mixtures that appear to be homogeneous are often found to be heterogeneous after microscopic examination. Milk, for example, appears to be homogeneous, but when examined under a microscope, it clearly consists of tiny globules of fat and protein dispersed in water. The components of heterogeneous mixtures can usually be separated by simple means. Solid-liquid mixtures such as sand in water or tea leaves in tea are readily separated by filtration, which consists of passing the mixture through a barrier, such as a strainer, with holes or pores that are smaller than the solid particles. In principle, mixtures of two or more solids, such as sugar and salt, can be separated by microscopic inspection and sorting. More complex operations are usually necessary, though, such as when separating gold nuggets from river gravel by panning. First solid material is filtered from river water; then the solids are separated by inspection. If gold is embedded in rock, it may have to be isolated using chemical methods.



Figure **5.1.2**: A Heterogeneous Mixture. Under a microscope, whole milk is actually a heterogeneous mixture composed of globules of fat and protein dispersed in water. Figure used with permission from Wikipedia

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. **Distillation** makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

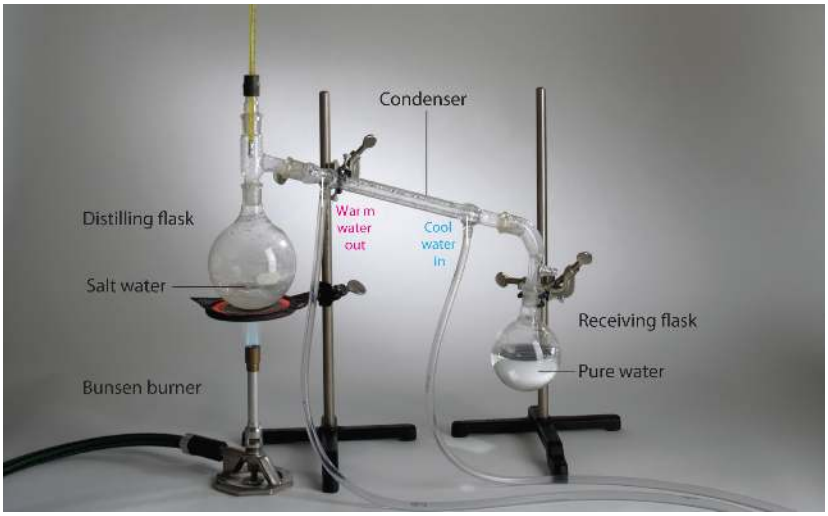


Figure **5.1.3**: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as

brandy or whiskey. (This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States!)

Crystallization separates mixtures based on differences in solubility, a measure of how much solid substance remains dissolved in a given amount of a specified liquid. Most substances are more soluble at higher temperatures, so a mixture of two or more substances can be dissolved at an elevated temperature and then allowed to cool slowly. Alternatively, the liquid, called the solvent, may be allowed to evaporate. In either case, the least soluble of the dissolved substances, the one that is least likely to remain in solution, usually forms crystals first, and these crystals can be removed from the remaining solution by filtration.



Figure **5.1.4**: The Crystallization of Sodium Acetate from a Concentrated Solution of Sodium Acetate in Water. The addition of a small “seed” crystal (a) causes the compound to form white crystals, which grow and eventually occupy most of the flask. Video can be found here: www.youtube.com/watch?v=BLq5NibwV5g

closeup of bulb flask containing liquid with many thin spike crystals radially emerging from the center.

Most mixtures can be separated into pure substances, which may be either elements or compounds. An **element**, such as gray, metallic sodium, is a substance that cannot be broken down into simpler ones by chemical changes; a **compound**, such as white, crystalline sodium chloride, contains two or more elements and has chemical and physical properties that are usually different from those of the elements of which it is composed. With only a few exceptions, a particular compound has the same elemental composition (the same elements in the same proportions) regardless of its source or history. The chemical composition of a substance is altered in a process called a **chemical change**. The conversion of two or more elements, such as sodium and chlorine, to a chemical compound, sodium chloride, is an example of a chemical change, often called a chemical reaction. Currently, about 118 elements are known, but millions of chemical compounds have been prepared from these 118 elements. The known elements are listed in the periodic table.

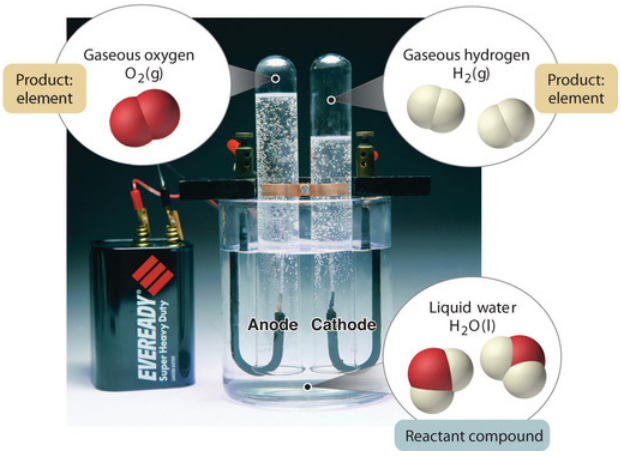


Figure **5.1.5**: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

a battery wired to an anode and cathode placed in a beaker filled with water. Two inverted test tubes are submerged in the water and placed over each of the electrodes to collect the gaseous products. Magnifying pointers show the molecular structure of water in the beaker as well as the hydrogen gas collected on the anode side and oxygen gas on the cathode side.



Different Definitions of Matter: Different Definitions of Matter, YouTube (opens in new window) [youtu.be]

In general, a reverse chemical process breaks down compounds into their elements. For example, water (a compound) can be decomposed into hydrogen and oxygen (both elements) by a process called electrolysis. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (Figure 5.1.5). A similar technique is used on a vast scale to obtain pure aluminum, an element, from its ores, which are mixtures of compounds. Because a great deal of energy is required for electrolysis, the cost of electricity is by far the greatest expense incurred in manufacturing pure aluminum. Thus recycling aluminum is both cost-effective and ecologically sound.

The overall organization of matter and the methods used to separate mixtures are summarized in Figure 5.1.6.

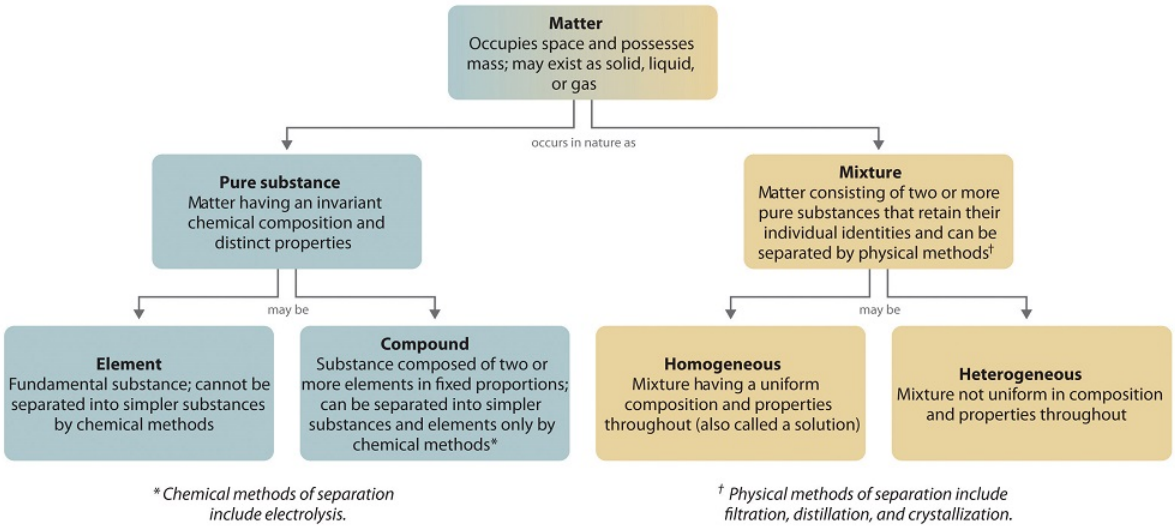


Figure 5.1.6: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 5.1.1

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

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

Given: a chemical substance

Asked for: its classification

Strategy:

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 5.1.1

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

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

Answer A

solution

Answer B

element

Answer C

heterogeneous mixture

Answer D

compound



Different Definitions of Changes: Different Definitions of Changes, YouTube(opens in new window) [youtu.be] (opens in new window)

Summary

Matter can be classified according to physical and chemical properties. Matter is anything that occupies space and has mass. The three states of matter are solid, liquid, and gas. A physical change involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of mixtures of pure substances, which can be homogeneous (uniform in composition) or heterogeneous (different regions possess different compositions and properties). Pure substances can be either chemical compounds or elements. Compounds can be broken down into elements by chemical reactions, but elements cannot be separated into simpler substances by chemical means. The properties of substances can be classified as either physical or chemical. Scientists can observe physical properties without changing the composition of the substance, whereas chemical properties describe the tendency of a substance to undergo chemical changes (chemical reactions) that change its chemical composition. Physical properties can be intensive or extensive. Intensive properties are the same for all samples; do not depend on sample size; and include, for example, color, physical state, and melting and boiling points. Extensive properties depend on the amount of material and include mass and volume. The ratio of two extensive properties, mass and volume, is an important intensive property called density.

Contributors and Attributions

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5.2: Phase Transitions - Melting, Boiling, and Subliming

Learning Objective

- Describe what happens during a phase change.
- Calculate the energy change needed for a phase change.

Substances can change phase—often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous.

The process of a solid becoming a liquid is called **melting** (an older term that you may see sometimes is *fusion*). The opposite process, a liquid becoming a solid, is called **solidification**. For any pure substance, the temperature at which melting occurs—known as the **melting point**—is a characteristic of that substance. It requires energy for a solid to melt into a liquid. Every pure substance has a certain amount of energy it needs to change from a solid to a liquid. This amount is called the **enthalpy of fusion (or heat of fusion)** of the substance, represented as ΔH_{fus}. Some ΔH_{fus} values are listed in Table **5.2.1**; it is assumed that these values are for the melting point of the substance. Note that the unit of ΔH_{fus} is kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{fus} is always tabulated as a positive number. However, it can be used for both the melting and the solidification processes, minding that melting is always endothermic (so ΔH will be positive), while solidification is always exothermic (so ΔH will be negative).

Table **5.2.1**: Enthalpies of Fusion for Various Substances

Substance (Melting Point)	ΔH_{fus} (kJ/mol)
Water (0°C)	6.01
Aluminum (660°C)	10.7
Benzene (5.5°C)	9.95
Ethanol (−114.3°C)	5.02
Mercury (−38.8°C)	2.29

Example 5.2.1

What is the energy change when 45.7 g of $\mathbf{H_2O}$ melt at 0°C?

Solution

The ΔH_{fus} of $\mathbf{H_2O}$ is 6.01 kJ/mol. However, our quantity is given in units of grams, not moles, so the first step is to convert grams to moles using the molar mass of $\mathbf{H_2O}$, which is 18.0 g/mol. Then we can use ΔH_{fus} as a conversion factor. Because the substance is melting, the process is endothermic, so the energy change will have a positive sign.

$$45.7\ \cancel{g\ H_2O} \times \frac{1\ \cancel{mol\ H_2O}}{18.0\ \cancel{g}} \times \frac{6.01 kJ}{\cancel{mol}} = 15.3\ kJ$$

Without a sign, the number is assumed to be positive.

Exercise 5.2.1

What is the energy change when 108 g of $\mathbf{C_6H_6}$ freeze at 5.5°C?

Answer

−13.8 kJ

During melting, energy goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. Hence melting is an **isothermal** process because a substance stays at the same temperature. Only when all of a substance is melted does additional energy go to changing its temperature.

What happens when a solid becomes a liquid? In a solid, individual particles are stuck in place because the intermolecular forces cannot be overcome by the energy of the particles. When more energy is supplied (e.g., by raising the temperature), there comes a point at which the particles have enough energy to move around, but not enough energy to separate. This is the liquid phase: particles are still in contact, but are able to move around each other. This explains why liquids can assume the shape of their containers: the particles move around and, under the influence of gravity, fill the lowest volume possible (unless the liquid is in a zero-gravity environment—see Figure **5.2.1**.



Figure **5.2.1**: Liquids and Gravity. (a) A liquid fills the bottom of its container as it is drawn downward by gravity and the particles slide over each other. (b) A liquid floats in a zero-gravity environment. The particles still slide over each other because they are in the liquid phase, but now there is no gravity to pull them down. Source: Photo on the left © Thinkstock. Photo on the right courtesy of NASA, http://www.nasa.gov/mission_pages/st...image_009.html.

The phase change between a liquid and a gas has some similarities to the phase change between a solid and a liquid. At a certain temperature, the particles in a liquid have enough energy to become a gas. The process of a liquid becoming a gas is called **boiling (or vaporization)**, while the process of a gas becoming a liquid is called **condensation**. However, unlike the solid/liquid conversion process, the liquid/gas conversion process is noticeably affected by the surrounding pressure on the liquid because gases are strongly affected by pressure. This means that the temperature at which a liquid becomes a gas, the **boiling point**, can change with surrounding pressure. Therefore, we define the **normal boiling point** as the temperature at which a liquid changes to a gas when the surrounding pressure is exactly 1 atm, or 760 torr. Unless otherwise specified, it is assumed that a boiling point is for 1 atm of pressure.

Like the solid/liquid phase change, the liquid/gas phase change involves energy. The amount of energy required to convert a liquid to a gas is called the **enthalpy of vaporization** (or heat of vaporization), represented as ΔH_{vap}. Some ΔH_{vap} values are listed in Table **5.2.2**; it is assumed that these values are for the normal boiling point temperature of the substance, which is also given in the table. The unit for ΔH_{vap} is also kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{vap} is also always tabulated as a positive number. It can be used for both the boiling and the condensation processes as long as you keep in mind that boiling is always endothermic (so ΔH will be positive), while condensation is always exothermic (so ΔH will be negative).

Table **5.2.1**: Enthalpies of Vaporization for Various Substances

Substance (Normal Boiling Point)	ΔH_{vap} (kJ/mol)
Water (100°C)	40.68
Bromine (59.5°C)	15.4
Benzene (80.1°C)	30.8
Ethanol (78.3°C)	38.6
Mercury (357°C)	59.23

Example 5.2.2

What is the energy change when 66.7 g of $Br_2(g)$ condense to a liquid at 59.5°C?

Solution

The ΔH_{vap} of Br_2 is 15.4 kJ/mol. Even though this is a condensation process, we can still use the numerical value of ΔH_{vap} as long as we realize that we must take energy out, so the ΔH value will be negative. To determine the magnitude of the energy change, we must first convert the amount of Br_2 to moles. Then we can use ΔH_{vap} as a conversion factor.

$$66.7\ \cancel{g\ Br_2} \times \frac{1\ \cancel{mol\ Br_2}}{159.8\ \cancel{g}} \times \frac{15.4 kJ}{\cancel{mol}} = 6.43\ kJ$$

Because the process is exothermic, the actual value will be negative: $\Delta H = -6.43$ kJ.

Exercise 5.2.2

What is the energy change when 822 g of $C_2H_5OH(\ell)$ boil at its normal boiling point of 78.3°C?

Answer

689 kJ

As with melting, the energy in boiling goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. So boiling is also an isothermal process. Only when all of a substance has boiled does any additional energy go to changing its temperature.

What happens when a liquid becomes a gas? We have already established that a liquid is composed of particles in contact with each other. When a liquid becomes a gas, the particles separate from each other, with each particle going its own way in space. This is how gases tend to fill their containers. Indeed, in the gas phase most of the volume is empty space; only about 1/1,000th of the volume is actually taken up by matter (Figure 5.2.1). It is this property of gases that explains why they can be compressed, a fact that is considered in Chapter 6.

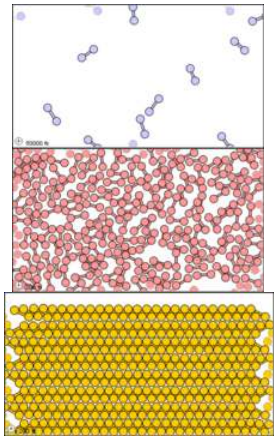


Figure 5.2.2: Sub-microscopic view of the diatomic molecules of the element bromine (a) in the gaseous state (above 58°C); (b) in liquid form (between -7.2 and 58.8°C); and (c) in solid form (below -7.2°C). As a solid, the molecules are fixed, but fluctuate. As a liquid, the molecules are in contact but are also able to move around each other. As a gas, most of the volume is actually empty space. The particles are not to scale; in reality, the dots representing the particles would be about 1/100th of the size depicted.

Under some circumstances, the solid phase can transition directly to the gas phase without going through a liquid phase, and a gas can directly become a solid. The solid-to-gas change is called **sublimation**, while the reverse process is called **deposition.** Sublimation is isothermal, like the other phase changes. There is a measurable energy change during sublimation—this energy change is called the **enthalpy of sublimation**, represented as ΔH_{sub}. The relationship between the ΔH_{sub} and the other enthalpy changes is as follows:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

As such, ΔH_{sub} is not always tabulated because it can be simply calculated from ΔH_{fus} and ΔH_{vap}.

There are several common examples of sublimation. A well-known product, dry ice, is actually solid CO_2. Dry ice is dry because it sublimes, with the solid bypassing the liquid phase and going straight to the gas phase. The sublimation occurs at temperature of −77°C, so it must be handled with caution. If you have ever noticed that ice cubes in a freezer tend to get smaller over time, it is because the solid water is very slowly subliming. "Freezer burn" isn't actually a burn; it occurs when certain foods, such as meats, slowly lose solid water content because of sublimation. The food is still good, but looks unappetizing. Reducing the temperature of a freezer will slow the sublimation of solid water.



Figure **5.2.3**: Freezer burn on a piece of beef. (Public Domain; RolloM.)

Chemical equations can be used to represent a phase change. In such cases, it is crucial to use phase labels on the substances. For example, the chemical equation for the melting of ice to make liquid water is as follows:

$$H_2O(s) \rightarrow H_2O(\ell)$$

No chemical change is taking place; however, a physical change is taking place.

Summary

- Phase changes can occur between any two phases of matter.
- All phase changes occur with a simultaneous change in energy.
- All phase changes are isothermal.

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CHAPTER OVERVIEW

6: Radioactivity

The major types of radioactivity include alpha particles, beta particles, and gamma rays. Fission is a type of radioactivity in which large nuclei spontaneously break apart into smaller nuclei.

Learning Objective

- Define and give examples of the major types of radioactivity.

We saw in Chapter 3 that atoms are composed of subatomic particles—protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of an atom, while electrons circle the nucleus in shells and subshells and account for an atom's size.

In Chapter 2, we also introduced the notation for succinctly representing an isotope of a particular atom:

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

The element in this example, represented by the symbol C, is carbon. Its atomic number, 6, is the subscript next to the symbol and is the number of protons in the atom. The mass number, the superscript next to the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 12, which means that the number of neutrons in the atom is 12 − 6 = 6 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neurons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen—$^{2}\mathrm{H}$ and $^{3}\mathrm{H}$—are given their own names and symbols: deuterium (D) and tritium (T), respectively.

Atomic theory in the nineteenth century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source being the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an **alpha particle**, which is symbolized by the Greek letter α. An alpha particle is composed of 2 protons and 2 neutrons and is the same as a helium nucleus. We often use:

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

to represent an alpha particle. It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by 2 (because of the loss of 2 protons), and its mass number decreases by 4 (because of the loss of 4 nuclear particles). We can represent the emission of an alpha particle with a chemical equation. For example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th}$$

Rather than calling this equation a chemical equation, we call it a **nuclear equation** to emphasize that the change occurs in an atomic nucleus. How do we know that a product of this reaction is \(\ce{^{90}_{231}T}\)? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means that we must have the same number of protons and neutrons on both sides of the nuclear equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose four nuclear particles of the original 235, there are 231 remaining. So we use subtraction to identify the isotope of the Th atom—in this case,

$$^{231}_{90}\mathrm{Th}$$

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example,

$$^{235}_{92}\text{U}$$

is the parent isotope, and

$$^{231}_{90}\text{Th}$$

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

Example 6.1

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 6.2

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

Answer

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

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

The second major type of radioactive emission is called a **beta particle**, symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a 1− charge. We can also represent a beta particle as e−10. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

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

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an "atomic number" of –1, equal to its charge.)

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called **gamma rays**, symbolized by the Greek letter γ. Gamma rays themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed *ionizing radiation*). For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

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

This may not seem like much energy, but if 1 mol of Rn atoms were to decay, the gamma ray energy would be 4.9×10^7 kJ!

Example 6.3

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 B-12,

$$^{12}_{5}\text{B}$$

while one of the products is B-12,

$$^{0}_{-1}\text{e}$$

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 6.4

Answer

$$^{133}_{43}\text{Tc} \rightarrow {}^{133}_{44}\text{Ru} + {}^{0}_{-1}\text{e} + \gamma$$

Alpha, beta, and gamma emissions have different abilities to penetrate matter. The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 6.1 summarizes the properties of the three main types of radioactive emissions.

Table 6.1 The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, H24	β $_{-1}^{0}$e	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1−	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called **spontaneous fission (or fission)**. Typically, the daughter isotopes produced by fission are a varied mix of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is

$$^{235}_{92}\text{Tc} \rightarrow {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 2\,{}^{1}_{0}\text{n}$$

where $_0^1n$ is a neutron. As with any nuclear process, the sums of the atomic numbers and mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208. (Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.)

Key Takeaways

- The major types of radioactivity include alpha particles, beta particles, and gamma rays.
- Fission is a type of radioactivity in which large nuclei spontaneously break apart into smaller nuclei.

6.1: Uses of Radioactive Isotopes

6.2: Half-Life

6.3: Unsafe Doses of Radiation

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6.1: Uses of Radioactive Isotopes

Learning Objective

- Learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful because either we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A **tracer** is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of carbon-14 to determine the steps involved in photosynthesis in plants. We know these steps because researchers followed the progress of carbon-14 throughout the process.

Radioactive Dating

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about $4.5 \times 10^9 y$. Many analyses like this, using a wide variety of isotopes, have indicated that age of the earth itself is over $4 \times 10^9 y$.

In another interesting example of radioactive dating, hydrogen-3 dating has been used to verify the stated vintages of some old fine wines.

One isotope, carbon-14, is particularly useful in determining the age of once-living artifacts. A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, albeit very low, level. Once a living thing dies, it no longer acquires carbon-14; as time passes the carbon-14 that was in the tissues decays. (The half-life of carbon-14 is 5,370 y.) If a once-living artifact is discovered and analyzed many years after its death and the remaining carbon-14 is compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (Figure **6.1.1** purported by some to be the burial cloth of Jesus Christ and composed of flax fibers, a type of plant) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.

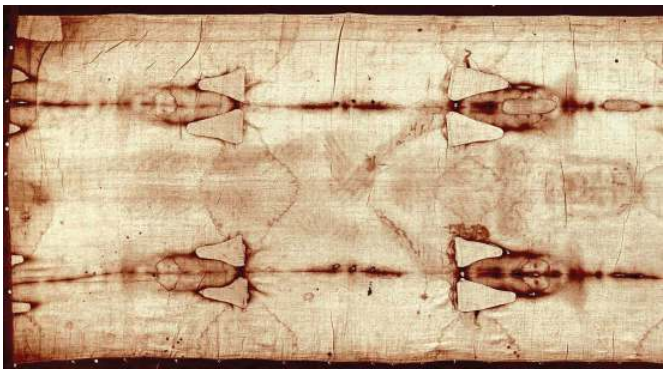


Figure **6.1.1**: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

Irradiation of Food

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, extending the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from coba . This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Medical Applications

Radioactive isotopes have numerous medical applications in diagnosing and treating illness and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure **6.1.1**). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of ^{131}I is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

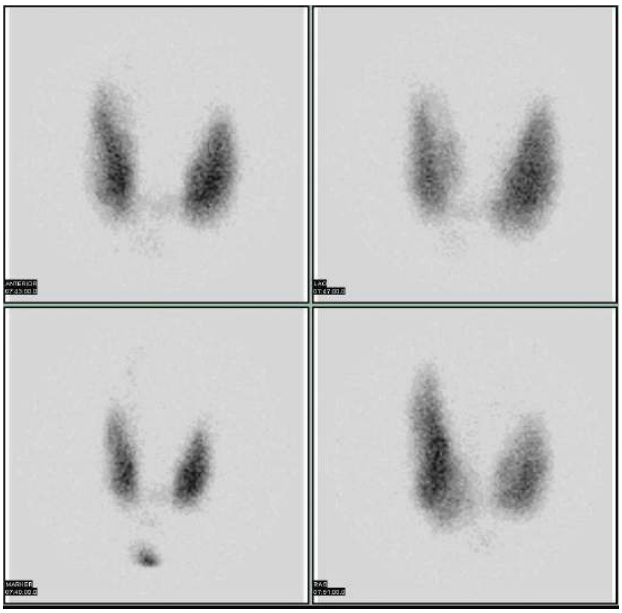


Figure **6.1.2**: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source: Scan courtesy of Myo Han, en.Wikipedia.org/wiki/File:Thyroid_scan.jpg.

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumor were detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less than 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect, but also to ease the pain of bone cancers. Table **6.1.1** lists several radioactive isotopes and their medical uses.

Table **6.1.1**: Some Radioactive Isotopes with Medical Applications

Isotope	Use
^{32}P	cancer detection and treatment, especially in eyes and skin
^{59}Fe	anemia diagnosis
^{60}Co	gamma ray irradiation of tumors
$^{99m}Tc^{*}$	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
^{131}I	diagnosis and treatment of thyroid function
^{133}Xe	lung imaging
^{198}Au	liver disease diagnosis
*The "m" means that it is a metastable form of this isotope of technetium.	

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

Food and Drink Application: Radioactivity in Wines

Wine lovers put some stock in *vintages*, or the years in which the wine grapes were grown before they were turned into wine. Wine can differ in quality depending on the vintage. Some wine lovers willingly pay much more for a bottle of wine with a certain vintage. But how does one verify that a bottle of wine was in fact part of a certain vintage? Is the label a fake? Is that stash of wine found in the basement of a French chateau really from the 1940s, or was it made in 2009?

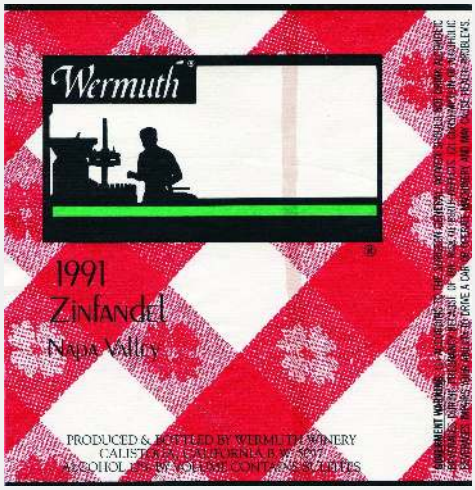


Figure **6.1.3**: A wine label. This wine label from a bottle of wine claims a vintage of 1991. Is the wine really from this vintage, or is it a fake? Radioactivity can help determine the answer. Source: Used by permission of Ralph E. Wermuth.

Cesium-137 is a radioactive isotope that has a half-life of 30.1 y. It was introduced into the atmosphere in the 1940s and 1950s by the atmospheric testing of nuclear weapons by several countries after World War II. A significant amount of cesium-137 was released during the Chernobyl nuclear disaster in 1986. As a result of this atmospheric contamination, scientists have precise measurements of the amount of cesium-137 available in the environment since 1950. Some of the isotope of cesium is taken up by living plants, including grape vines. Using known vintages, oenologists (wine scientists) can construct a detailed analysis of the cesium-137 of various wines through the years.

The verification of a wine's vintage requires the measurement of the activity of cesium-137 in the wine. By measuring the current activity of cesium-137 in a sample of wine (the gamma rays from the radioactive decay pass through glass wine bottles easily, so there's no need to open the bottle), comparing it to the known amount of cesium-137 from the vintage, and taking into account the passage of time, researchers can collect evidence for or against a claimed wine vintage.

> Before about 1950, the amount of cesium-137 in the environment was negligible, so if a wine dated before 1950 shows any measurable cesium-137 activity, it is almost surely a fake, so do not shell out lots of money for it! It may be a good wine, but it is almost definitely not over 60 years old.

Summary

Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and preservation of food.

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6.2: Half-Life

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life**, 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.

Consider the following example. Suppose we have 100.0 g of tritium (a radioactive isotope of hydrogen). It has a half-life of 12.3 y. After 12.3 y, half of the sample will have decayed from hydrogen-3 to helium-3 by emitting a beta particle, so that only 50.0 g of the original tritium remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining tritium will have decayed, leaving 25.0 g of tritium. After another 12.3 y—now a total of 36.9 y—another half of the remaining tritium will have decayed, leaving 12.5 g. This sequence of events is illustrated in Figure 6.2.1 - Radioactive Decay.

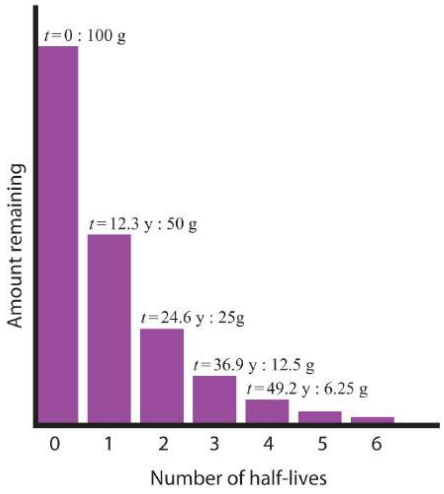


Figure **6.2.1** Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

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

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

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

Example 6.2.1

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 we use the previous expression n = 4. Substituting and solving results in the following:

$$\begin{aligned}\textbf{amount remaining} &= 5.00\,g \times \left(\frac{1}{2}\right)^{4} \\ &= 5.00\,g \times \left(\frac{1}{16}\right) \\ &= 0.313\,g\end{aligned}$$

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

Exercise 6.2.1

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

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table **6.2.1** - Half-Lives of Various Isotopes, lists the half-lives of some isotopes.

Table **6.2.1** Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^{8} y
^{238}U	4.47×10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Chemistry is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. The following table summarizes radioactivity in the normal human body.

Table with four columns and eight rows. The first column on the left is labeled as Radioactive Isotope, underneath in the rows has radioactive isotopes. The second column is labeled as Half-Life (y), underneath in the rows has half-lives. The third column is labeled as Isotope Mass in the Body (g), underneath in the rows has isotope masses. The fourth column on right is labeled as Activity in the Body (decays/s), underneath in the rows has the activities in the body as the decays.

Radioactive Isotope	Half-Life (y)	Isotope Mass in the Body (g)	Activity in the Body (decays/s)
^{40}K	1.26×10^{9}	0.0164	4,340
^{14}C	5,730	1.6×10^{-8}	3,080
^{87}Rb	4.9×10^{10}	0.19	600
^{210}Pb	22.3	5.4×10^{-10}	15
^{3}H	12.3	2×10^{-14}	7
^{238}U	4.47×10^{9}	1×10^{-4}	5
^{228}Ra	5.76	4.6×10^{-14}	5
^{226}Ra	1,620	3.6×10^{-11}	3

The average human body experiences about 8,000 radioactive decays.

Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

What if the elapsed time is not an exact number of half-lives? We can still calculate the amount of material we have left, but the equation is more complicated. The equation is

$$\text{amount remaining} = (\text{amount initial}) \times e^{-0.693t/t_{1/2}}$$

where e is the base of natural logarithms (2.71828182…), t is the elapsed time, and $t_{1/2}$ is the half-life of the radioactive isotope. The variables t and $t_{1/2}$ should have the same units of time, and you may need to make sure you know how to evaluate natural-logarithm powers on your calculator (for many calculators, there is an "inverse logarithm" function that you can use; consult your instructor if you are not sure how to use your calculator). Although this is a more complicated formula, the length of time t need not be an exact multiple of half-lives.

Example 6.2.2

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 60.0 s?

Solution

Although similar to Example 3, the amount of time is not an exact multiple of a half-life. Here we identify the initial amount as 5.00 g, t = 60.0 s, and $t_{1/2}$ = 11.0 s. Substituting into the equation:

$$\text{amount remaining} = (5.00\text{ g}) \times e^{-(0.693)(60.0\text{ s})/11.0\text{ s}}$$

Evaluating the exponent (and noting that the s units cancel), we get

$$\text{amount remaining} = (5.00\text{ g}) \times e^{-3.78}$$

Solving, the amount remaining is 0.114 g. (You may want to verify this answer to confirm that you are using your calculator properly.)

? Exercise 6.2.2

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 100.0 y?

Answer

0.189 g

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

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6.3: Unsafe Doses of Radiation

Radiation Leaks at Fukushima Dose Workers. After everyone else was evacuated from the Fukushima Daiichi nuclear power plant following the tsunami disaster, around fifty workers were left behind to cool the spent fuel rods and overheating nuclear reactor. These workers pumped seawater on the reactors in a desperate attempt to bring them back under control, meanwhile exposing the workers to dangerous radiation. 1

How is radiation exposure measured and what is considered dangerous? Well, there are different methods to measure exposure to ionizing radiation and units to express these measurements. One unit used is “grays per hour” which describes the absorbed dose rate in the air which describes the intensity of gamma radiation in the air. This in turn can be translated to radiation dose, or gray (Gy) which is equal to one joule of radiation energy that is absorbed per kilogram of organ or tissue weight. Before gray was used, the unit rad was; so that 1 Gy = 100 rads. All radiation is not created equal, some forms are more harmful that others so to incorporate that factor (known as the “radiation weighting factor), radiation dose is expressed as equivalent dose in units called sievert (Sv). That makes one gray air dose equal to 0.7 Sv tissue dose. Sievert is the SI unit of radiation dose; SI meaning the International System of units used by the scientific community in order to facilitate communication. Another unit of radiation dose that is sometimes used is rem which is based on the unit rad; 1 Sv is equal to 100 rem.2

What is considered a dangerous dose of radiation? According to the ICRP (International Commission on Radiological Protection) the recommended annual dose limit for the general public is 1 mSv or 0.001 Sv. Radiation workers however, can be exposed to 50 mSv in any given year but average only 20 mSv per year in a 5 year period. Exposure to 10 Sv will most like result in death within days or weeks and at 1 Sv, a person runs the risk of cancer later in life as well as temporary radiation sickness and a drop in white blood cell count. 2 Sv is high enough to cause immediate radiation sickness which results in skin redness or burns, hair loss and nausea. At 3 Sv, the initial symptoms of radiation sickness can also include vomiting and diarrhea and progress to a period of serious illness including appetite loss, fatigue, fever, gastrointestinal problems, possible seizures or coma and may last from hours to months.3

There are three ways to reduce radiation exposure; reduce the amount of time exposed to radiation, increase the distance from the source of radiation, and wear protective clothing to shield the radiation. Radiation limits are designed to be “as low as reasonable achievable” or ALARA, and are very conservative as you can see, many times below the level that would cause radiation sickness.4

Questions:

1. The standard legal limit for annual radiation dose for radiation workers is 50 mSv but it was raised to 250 mSv so that the 50 workers could continue to cool down the reactors. If radiation reached levels of 400 mSv/hr at Fukishima. How long would it take for an unprotected radiation worker to receive the 250 mSv?

2. Readings at the border of the nuclear plant site were 6 mSv/hr. How long would it take for a member of the general public to absorb 10 mSv of radiation?
3. How many mrem is 3 Sv?
4. The commonly accepted value for increased risk of cancer is 4% per Sv. If a person was exposed to 50 mSv every year for 20 years, what would his increased risk for cancer be?
5. People are exposed to 350 mrem of background radiation per year so the radiation dose guidelines refer to additional radiation. If you had a CAT scan that delivers a dose of 4.1 mSv, what is your total radiation dose for that year in Sv?
6. If you lived near a nuclear power plant, what precautions could you take to limit your exposure to radiation in the event of an accident? Answers to Radiation Dose Questions

1. Biello, David, Workers Battle Fukushima Nuclear Crisis at Personal Risk, Scientific American, March 16, 2011 online http://www.scientificamerican.com/article.cfm?id=fukushima-workers 2. McGill Radiation Safety Policy Manual › 3. Radiation dose limit, McGill University, www.mcgill.ca/ehs/radiation/manual/3/ 3. Bai, Nina, How Radiation Affects Health, Scientific American, March 15, 2011 online http://www.scientificamerican.com/article.cfm?id=how-radiation-threatens-health 4. Biello, David, Workers Battle Fukushima Nuclear Crisis at Personal Risk, Scientific American, March 16, 2011 online http://www.scientificamerican.com/article.cfm?id=fukushima-workers

From ChemPRIME: 19.10: Units of Radiation Dose

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CHAPTER OVERVIEW

7: Chemical Bonds

Diamond is the hardest natural material known on Earth. Yet diamond is just pure carbon. What is special about this element that makes diamond so hard? Bonds. Chemical bonds.

In a perfect diamond crystal, each C atom makes four connections—bonds—to four other C atoms in a three-dimensional matrix. Four is the greatest number of bonds that is commonly made by atoms, so C atoms maximize their interactions with other atoms. This three-dimensional array of connections extends throughout the diamond crystal, making it essentially one large molecule. Breaking a diamond means breaking every bond at once. Also, the bonds are moderately strong. There are stronger interactions known, but the carbon-carbon connection is fairly strong itself. Not only does a person have to break many connections at once, but the bonds are also strong connections from the start.



Diamond is the hardest known natural substance and is composed solely of the element carbon. (CC SA-BY 3.0; Mario Sarto).

There are other substances that have bonding arrangements similar to diamond. Silicon dioxide and boron nitride have some similarities, but neither of them comes close to the ultimate hardness of diamond.

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7.1: Lewis Electron Dot Diagrams

Learning Objective

- Draw a Lewis electron dot diagram for an atom or a monatomic ion.

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

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

$$\mathbf{H}\cdot$$

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

$$\dot{\mathbf{H}} \quad \textit{or} \quad \cdot\mathbf{H} \quad \textit{or} \quad \underset{\cdot}{\mathbf{H}}$$

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

$$\mathbf{He:}$$

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

$$\mathbf{Li}\cdot$$

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

$$\mathbf{Be:}$$

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

$$\dot{\mathbf{B}}\mathbf{e:}$$

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

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

$$\cdot\dot{\mathbf{C}}\mathbf{:}$$

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

$$\cdot\dot{\underset{\cdot}{\mathbf{N}}}\mathbf{:}$$

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

$$\cdot\ddot{\underset{\cdot}{\mathbf{O}}}\mathbf{:}$$

Fluorine and neon have seven and eight dots, respectively:





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

Example 7.1.1

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:



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:



Exercise 7.1.1

What is the Lewis electron dot diagram for each element?

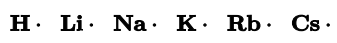
a. phosphorus
b. argon

Answer

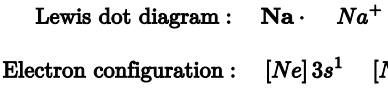




Elements in the same column of the periodic table have similar Lewis electron dot diagrams because they have the same valence shell electron configuration. The electron dot diagrams for the first column of elements are as follows:



Monatomic ions are atoms that have either lost (for cations) or gained (for anions) electrons. Electron dot diagrams for ions are the same as for atoms, except that some electrons have been removed for cations, while some electrons have been added for anions. Thus, in comparing the electron configurations and electron dot diagrams for the Na atom and the Na^+ ion, we note that the Na atom has a single valence electron in its Lewis diagram, while the Na^+ ion has lost that one valence electron:



In making cations, electrons are first lost from the *highest numbered shell*, not necessarily the last subshell filled. For example, in going from the neutral Fe atom to the Fe^{2+} ion, the Fe atom loses its two 4*s* electrons first, not its 3*d* electrons, despite the fact that the 3*d* subshell is the last subshell being filled. Thus, we have

$$\textbf{Lewis dot diagram :} \quad \textbf{Fe} : \quad Fe^{2+}$$

$$\textbf{Electron configuration :} \quad [Ar]\,4s^2 3d^6 \quad [Ar]\,3d^6$$

Anions have extra electrons when compared to the original atom. Here is a comparison of the Cl atom with the Cl^- ion:

$$\textbf{Lewis dot diagram :} \quad :\ddot{\underset{\cdot\cdot}{\text{Cl}}}\cdot \quad :\ddot{\underset{\cdot\cdot}{\text{Cl}}}:^-$$

$$\textbf{Electron configuration :} \quad [Ne]\,3s^2 3p^5 \quad [Ne]\,3s^2 3p^6$$

Example 7.1.2

What is the Lewis electron dot diagram for each ion?

a. Ca^{2+}
b. O^{2-}

Solution

a. Having lost its two original valence electrons, the Lewis electron dot diagram is simply: Ca^{2+}
b. The O^{2-} ion has gained two electrons in its valence shell, so its Lewis electron dot diagram is as follows:

$$:\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-}$$

Exercise 7.1.2

The electronic configuration of the thallium ion is $6s^2 4f^{14} 5d^{10}$. What is the Lewis electron dot diagram for the Tl^+ ion?

Answer

$$\textbf{Tl} :^+$$

Summary

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis electron dot diagrams for ions have less (for cations) or more (for anions) dots than the corresponding atom.

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7.1.1: Lewis Dot and Bonding

Learning Objectives

- Realize that valence electrons can be represented by dots.
- Know that there are two types of bonding: ionic and covalent.
- Know that ionic bonding involves a metal and a nonmetal with a transfer of electrons.
- Know that covalent bonding involves two nonmetals or a metalloid with a nonmetal sharing electrons.

Bonding (Ionic and Covalent Basics)

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 stabile 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. A few examples of real-world ionic compounds would be NaCl (table salt) and NaF (active ingredient in toothpaste).



Figure **7.1.1.1**: NaCl crystals. (Public Domain; NASA).

If two nonmetals interact, then a covalent bond will result. The connection that forms is due to each atom sharing it(s) valence electron(s). In this type of bonding, each atom (except for H, B, and Be) obtains an octet and becomes stable. Metalloids and nonmetals can bond to form covalent compounds as well. Solid covalent compound are not crystalline in texture. Unlike ionic compounds. covalent compounds can be liquids or even gases.



Figure **7.1.1.2**: Covalent compounds NO_2 and N_2O_4 contained in glass bottles. Image taken from: commons.wikimedia.org/wiki/File:NO2-N2O4.jpg

Table **7.1.1.1**: Comparing ionic and covalent compounds

Ionic Bonding	Covalent Bonding
Metal/nonmetal combination	nonmetal/nonmetal or metalloid/nonmetal combination
Metal loses valence electrons and nonmetal gains up to eight.	Both elements share valence electrons to achieve stability
Individual species have cation/anion charges	No charges are present in these compounds
All ionic compounds are solids	Covalent compounds can be solid, liquid, or gas.
Examples could include: Li_2CO_3, Fe_2O_3, and $MgSO_4$	Examples include: CO_2, H_2O, and CH_3CH_2OH

Lewis Symbols

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. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons. Lewis knew that incorporating models into his teaching would enable students to visualize chemical bonding easier. Gilbert Lewis was known for his interactive teaching methods and his interest in student success. Unfortunately, his nervous personality limited his ability to lecture in front of large groups of people.

Regarding his research, Lewis constructed his own theory to explain the nature of acids and bases. He was the first to synthesize D_2O (heavy water) and wrote numerous textbooks for his courses. In World War I, he served as a Major in the Gas Service unit of the American Army. He trained over 200 soldiers a week on how to adequately protect themselves from gas warfare. From these efforts, he helped reduce fatalities due to chemical gas exposures and was awarded the Distinguish Service Medal in 1922.

Lewis was nominated over thirty times for the Nobel Prize. He never received this award and does not have an element named in honor of him. For more on Gilbert Lewis, click on this link.

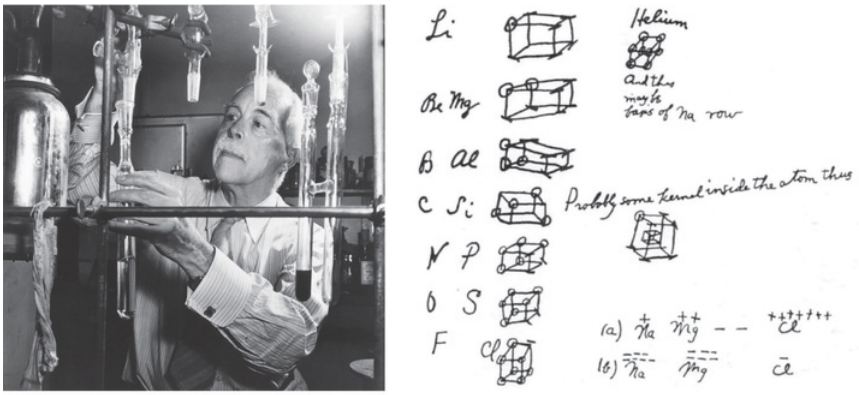


Figure 7.1.1.3: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

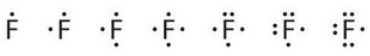
Lewis Dot symbols

- convenient representation of valence electrons
- allows scientists to keep track of valence electrons during bond formation
- consists of the chemical 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:



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



The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols and electron configurations (not a topic for this course) for the elements in period 2 are given in Table **7.1.1.2**.

***Table* 7.1.1.2:** *Lewis Dot Symbols for the Elements in Period 2*

Group	1	2	13	14	15	16	17	18
Electron Configuration	$[He]2s^1$	$[He]2s^2$	$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	$[He]2s^22p^4$	$[He]2s^22p^5$	$[He]2s^22p^6$
Lewis Dot Symbol	Li ·	·Be·	· B ·	· C ·	· N ·	: O ·	: F ·	:Ne:

Ionic compounds are produced when a metal bonds with a nonmetal. Stability is achieved for both atoms once the transfer of electrons has occurred. The image below shows how sodium and chlorine bond to form the compound sodium chloride. Unlike a sodium atom, the resulting compound is not explosive and less corrosive than chlorine. Ionic bonding can be viewed by noting the donation of valence electrons from a metal atom to a nonmetal atom by using the Bohr model. From this theory, we will move on the Lewis structure with an understanding that metals will always lose valence electrons and nonmetals will gain up to eight in order to form stable compounds.

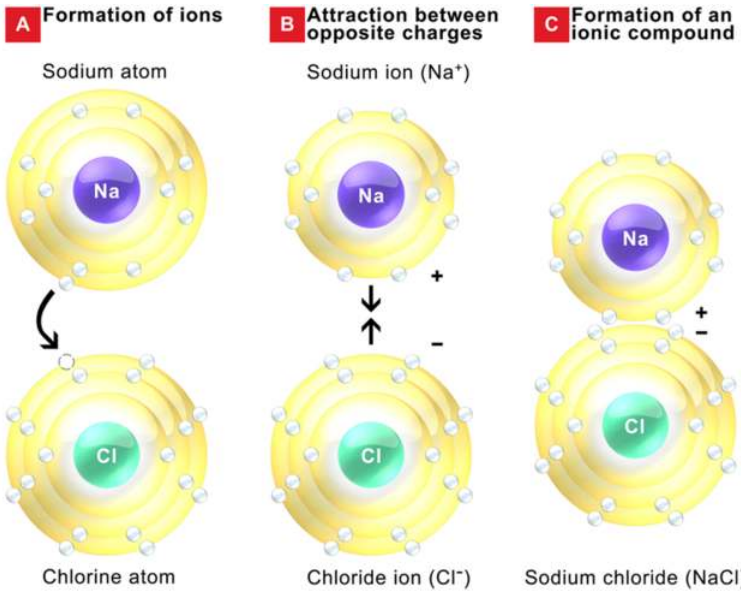


Figure **7.1.1.4**: Formation of an ionic bond between sodium and chlorine. Image courtesy of By BruceBlaus - Own work, CC BY-SA 4.0, commons.wikimedia.org/w/inde...curid=44968540

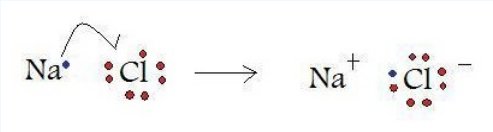
Rules for Drawing IOnic Lewis structures

When drawing Lewis structures for compounds formed from the combination of a metal/nonmetal, use the list of rules shown below:

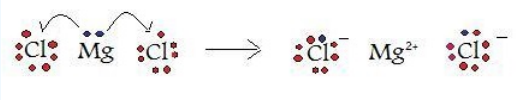
a. Locate the elements of interest and recall how many valence electrons each species has.
b. Draw dots around each element individually.
c. To obtain successful octets, the metal must transfer all of its valence electrons to the nonmetal.

d. At this point, the metal should have no electrons around it. In addition, the nonmetal will have an octet. If this does not occur, then refer to step e.
e. Additional atoms of the same two elements may be brought in to accomplish rules a-c.
f. **Cation and anion charges must be on Lewis structure to receive full credit (this is an ionic compound).**
g. To check structure, quickly write a formula for the ionic compound. This involves crossing down the charges diagonally and losing signs. You must reduce subscripts if they are divisible by a factor.

Example 7.1.1.1: Chloride Salts



In this example, 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. Only one atom of each element is needed to obtain a stable compound.



In this example, the magnesium atom is donating both of its valence electrons to chlorine atoms. Each chlorine atom can only accept 1 electron before it can achieve an octet; therefore, 2 atoms of chlorine are required to accept the 2 electrons donated by the magnesium. Notice that the net charge of the compound is 0. This Lewis structure requires two anions per one cation to produce a stable compound.

For more rigorous examples, access the CHM101 Furman moodle page (chapter 4 documents), to view a lightboard video of your instructor.

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7.2: Ions and Ionic Compounds

Learning Objectives

- Know how ions form.
- Learn the characteristic charges that ions have.
- Construct a proper formula for an ionic compound.
- Generate a proper name for an ionic compound.

So far, we have discussed elements and compounds that are electrically neutral. They have the same number of electrons as protons, so the negative charges of the electrons are balanced by the positive charges of the protons. However, this is not always the case. Electrons can move from one atom to another; when they do, species with overall electric charges are formed. Such species are called ions. Species with overall positive charges are termed **cations**, while species with overall negative charges are called **anions**. Remember that ions are formed only when *electrons* move from one atom to another; a proton never moves from one atom to another. Compounds formed from positive and negative ions are **ionic compounds**.

Individual atoms can gain or lose electrons. When they do, they become *monatomic* ions. When atoms gain or lose electrons, they usually gain or lose a characteristic number of electrons and so take on a characteristic overall charge. Table 7.2.1 lists some common ions in terms of how many electrons they lose (making cations) or gain (making anions). There are several things to notice about the ions in Table 7.2.1. First, each element that forms a cation is a metal, except for one (hydrogen), while each element that forms an anion is a nonmetal. This is actually one of the chemical properties of metals and nonmetals: metals tend to form cations, while nonmetals tend to form anions. Second, most atoms form ions of a single characteristic charge. When sodium atoms form ions, they always form a 1+ charge, never a 2+ or 3+ or even 1− charge. Thus, if you commit the information in Table **7.2.1** to memory, you will always know what charges most atoms form.

Table **7.2.1**: Monatomic Ions of Various Charges

Ions formed by losing a single electron	H^+
Na^+	
K^+	
Rb^+	
Ag^+	
Au^+	
Ions formed by losing two electrons	Mg^{2+}
	Ca^{2+}
	Sr^{2+}
	Fe^{2+}
	Co^{2+}
	Ni^{2+}
	Cu^{2+}
	Zn^{2+}
	Sn^{2+}
	Hg^{2+}
	Pb^{2+}
Ions formed by losing three electrons	Sc^{3+}
	Fe^{3+}
	Co^{3+}
	Ni^{3+}
	Au^{3+}
	Al^{3+}
	Cr^{3+}
Ions formed by losing four electrons	Ti^{4+}
	Sn^{4+}
	Pb^{4+}
Ions formed by gaining a single electron	F^-
	Cl^-
	Br^-
	I^-
Ions formed by gaining two electrons	O^{2-}
	S^{2-}
	Se^{2-}
Ions formed by gaining three electrons	N^{3-}
	P^{3-}

Third, there are some exceptions to the previous point. A few elements, all of which are metals, can form more than one possible charge. For example, iron atoms can form 2+ cations or 3+ cations. Cobalt is another element that can form more than one possible charged ion (2+ and 3+), while lead can form 2+ or 4+ cations. Unfortunately, there is little understanding which two charges a metal atom may take, so it is best to just memorize the possible charges a particular element can have.

Note the convention for indicating an ion. The magnitude of the charge is listed as a right superscript next to the symbol of the element. If the charge is a single positive or negative one, the number 1 is not written; if the magnitude of the charge is greater than 1, then the number is written *before* the + or − sign. An element symbol without a charge written next to it is assumed to be the uncharged atom.

Naming an ion is straightforward. For a cation, simply use the name of the element and add the word *ion* (or if you want to be more specific, add *cation*) after the element's name. So Na^+ is the sodium ion; Ca^{2+} is the calcium ion. If the element has more than one possible charge, the value of the charge comes after the element name and before the word *ion*. Thus, Fe^{2+} is the iron two ion, while Fe^{3+} is the iron three ion. In print, we use roman numerals in parentheses to represent the charge on the ion; so these two iron ions would be represented as the iron(II) cation and the iron(III) cation, respectively.

For a monatomic anion, use the stem of the element name and append the suffix *-ide* to it, and then add *ion*. This is similar to how we named molecular compounds. Thus, Cl^- is the chloride ion, and N^{3-} is the nitride ion.

Example 7.2.1

Name each species.

a. O^{2-}
b. Co
c. Co^{2+}

Solution

a. This species has a 2− charge on it, so it is an anion. Anions are named using the stem of the element name with the suffix *-ide* added. This is the oxide anion.
b. Because this species has no charge, it is an atom in its elemental form. This is cobalt.
c. In this case, there is a 2+ charge on the atom, so it is a cation. We note from Table **7.2.1** that cobalt cations can have two possible charges, so the name of the ion must specify which charge the ion has. This is the cobalt(II) cation.

Exercise 7.2.1

Name each species.

a. P^{3-}
b. Sr^{2+}

Answers

a. the phosphide anion
b. the strontium cation

Ionic Formulas

Chemical formulas for ionic compounds are called ionic formulas. A proper ionic formula has a cation and an anion in it; an ionic compound is never formed between two cations only or two anions only. The key to writing proper ionic formulas is simple: the total positive charge must balance the total negative charge. Because the charges on the ions are characteristic, sometimes we have to have more than one of a cation or an anion to balance the overall positive and negative charges. It is conventional to use the lowest ratio of ions that are needed to balance the charges.

For example, consider the ionic compound between Na^+ and Cl^-. Each ion has a single charge, one positive and one negative, so we need only one ion of each to balance the overall charge. When writing the ionic formula, we follow two additional conventions: (1) write the formula for the cation first and the formula for the anion second, but (2) do not write the charges on the ions. Thus, for

the compound between Na^+ and Cl^-, we have the ionic formula NaCl (Figure **7.2.1**). The formula Na_2Cl_2 also has balanced charges, but the convention is to use the lowest ratio of ions, which would be one of each. (Remember from our conventions for writing formulas that we do not write a 1 subscript if there is only one atom of a particular element present.) For the ionic compound between magnesium cations (Mg^{2+}) and oxide anions (O^{2-}), again we need only one of each ion to balance the charges. By convention, the formula is MgO.



Figure **7.2.1**: The ionic compound **NaCl** is table salt and is very common. (Public Domain; Pexels.)

For the ionic compound between Mg^{2+} ions and Cl^- ions, we now consider the fact that the charges have different magnitudes: 2+ on the magnesium ion and 1− on the chloride ion. To balance the charges with the lowest number of ions possible, we need to have two chloride ions to balance the charge on the one magnesium ion. Rather than write the formula MgClCl, we combine the two chloride ions and write it with a 2 subscript: $MgCl_2$.

What is the formula $MgCl_2$ telling us? There are two chloride ions in the formula. Although chlorine as an element is a diatomic molecule, Cl_2, elemental chlorine is not part of this ionic compound. The chlorine is in the form of a negatively charged *ion*, not the neutral *element*. The 2 subscript is in the ionic formula because we need two Cl^- ions to balance the charge on one Mg^{2+} ion.

✔ Example 7.2.2

Write the proper ionic formula for each of the two given ions.

a. Ca^{2+} and Cl^-
b. Al^{3+} and F^-
c. Al^{3+} and O^{2-}

Solution

a. We need two Cl^- ions to balance the charge on one Ca^{2+} ion, so the proper ionic formula is $CaCl_2$.
b. We need three F^- ions to balance the charge on the Al^{3+} ion, so the proper ionic formula is AlF_3.
c. With Al^{3+} and O^{2-}, note that neither charge is a perfect multiple of the other. This means we have to go to a least common multiple, which in this case will be six. To get a total of 6+, we need two Al^{3+} ions; to get 6−, we need three O^{2-} ions. Hence the proper ionic formula is Al_2O_3.

? Exercise 7.2.2

Write the proper ionic formulas for each of the two given ions.

a. Fe^{2+} and S^{2-}
b. Fe^{3+} and S^{2-}

Answers

a. FeS
b. Fe_2S_3

Naming ionic compounds is simple: combine the name of the cation and the name of the anion, in both cases omitting the word *ion*. *Do not use numerical prefixes if there is more than one ion necessary to balance the charges.* NaCl is sodium chloride, a combination of the name of the cation (sodium) and the anion (chloride). MgO is magnesium oxide. $MgCl_2$ is magnesium chloride —*not* magnesium dichloride.

When naming ionic compounds whose cations can have more than one possible charge, we must also include the charge, in parentheses and in roman numerals, as part of the name. Hence FeS is iron(II) sulfide, while Fe_2S_3 is iron(III) sulfide. Again, no numerical prefixes appear in the name. The number of ions in the formula is dictated by the need to balance the positive and negative charges.

Example 7.2.3

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. Co_2O_3

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride. It is *not* calcium(II) chloride, because calcium forms only one cation when it forms an ion, and it has a characteristic charge of 2+.
b. The name of this ionic compound is aluminum fluoride.
c. 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.

Exercise 7.2.3

Name each ionic compound.

a. Sc_2O_3
b. AgCl

Answers

a. scandium oxide
b. silver chloride

How do you know whether a formula—and by extension, a name—is for a molecular compound or for an ionic compound? Molecular compounds form between nonmetals and nonmetals, while ionic compounds form between metals and nonmetals. The periodic table can be used to determine which elements are metals and nonmetals.

There also exists a group of ions that contain more than one atom. These are called **polyatomic ions**. Table 7.2.2 lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as ***oxyanions***. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge.

Table 7.2.2: Common Polyatomic Ions

Name	Formula and Charge		Name	Formula and Charge
ammonium	NH_4^+		hydroxide	OH^-
acetate	$C_2H_3O_2^-$, or CH_3COO^-		nitrate	NO_3^-
bicarbonate (hydrogen carbonate)	HCO_3^-		nitrite	NO_2^-
bisulfate (hydrogen sulfate)	HSO_4^-		peroxide	O_2^{2-}
carbonate	CO_3^{2-}		perchlorate	ClO_4^-
chlorate	ClO_3^-		phosphate	PO_4^{3-}
chromate	CrO_4^{2-}		sulfate	SO_4^{2-}
cyanide	CN^-		sulfite	SO_3^{2-}
dichromate	$Cr_2O_7^{2-}$		triiodide	I_3^-

The naming of ionic compounds that contain polyatomic ions follows the same rules as the naming for other ionic compounds: simply combine the name of the cation and the name of the anion. Do not use numerical prefixes in the name if there is more than one polyatomic ion; the only exception to this is if the name of the ion itself contains a numerical prefix, such as dichromate or triiodide.

Writing the formulas of ionic compounds has one important difference. If more than one polyatomic ion is needed to balance the overall charge in the formula, enclose the formula of the polyatomic ion in parentheses and write the proper numerical subscript to the right and *outside* of the parentheses. Thus, the formula between calcium ions, Ca^{2+}, and nitrate ions, NO_3^-, is properly written $Ca(NO_3)_2$, not $CaNO_{32}$ or CaN_2O_6. Use parentheses where required. The name of this ionic compound is simply calcium nitrate.

✔ Example 7.2.4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and S^{2-}
b. Al^{3+} and PO_4^{3-}
c. Fe^{2+} and PO_4^{3-}

Solution

a. Because the ammonium ion has a 1+ charge and the sulfide ion has a 2− charge, we need two ammonium ions to balance the charge on a single sulfide ion. Enclosing the formula for the ammonium ion in parentheses, we have $(NH_4)_2S$. The compound's name is ammonium sulfide.
b. Because the ions have the same magnitude of charge, we need only one of each to balance the charges. The formula is $AlPO_4$, and the name of the compound is aluminum phosphate.
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+, we need three iron(II) ions, and to get 6−, we need two phosphate ions. The proper formula is $Fe_3(PO_4)_2$, and the compound's name is iron(II) phosphate.

? Exercise 7.2.4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and PO_4^{3-}
b. Co^{3+} and NO_2^-

Answers

a. $(NH_4)_3PO_4$, ammonium phosphate

b. $Co(NO_2)_3$, cobalt(III) nitrite

Food and Drink Application: Sodium in Your Food

The element sodium, at least in its ionic form as Na^+, is a necessary nutrient for humans to live. In fact, the human body is approximately 0.15% sodium, with the average person having one-twentieth to one-tenth of a kilogram in their body at any given time, mostly in fluids outside cells and in other bodily fluids.

Sodium is also present in our diet. The common table salt we use on our foods is an ionic sodium compound. Many processed foods also contain significant amounts of sodium added to them as a variety of ionic compounds. Why are sodium compounds used so much? Usually sodium compounds are inexpensive, but, more importantly, most ionic sodium compounds dissolve easily. This allows processed food manufacturers to add sodium-containing substances to food mixtures and know that the compound will dissolve and distribute evenly throughout the food. Simple ionic compounds such as sodium nitrite ($NaNO_2$) are added to cured meats, such as bacon and deli-style meats, while a compound called sodium benzoate is added to many packaged foods as a preservative. Table **7.2.3** is a partial list of some sodium additives used in food. Some of them you may recognize after reading this chapter. Others you may not recognize, but they are all ionic sodium compounds with some negatively charged ion also present.

Table **7.2.3**: Some Sodium Compounds Added to Food

Sodium Compound	Use in Food
Sodium acetate	preservative, acidity regulator
Sodium adipate	food acid
Sodium alginate	thickener, vegetable gum, stabilizer, gelling agent, emulsifier
Sodium aluminum phosphate	acidity regulator, emulsifier
Sodium aluminosilicate	anti-caking agent
Sodium ascorbate	antioxidant
Sodium benzoate	preservative
Sodium bicarbonate	mineral salt
Sodium bisulfite	preservative, antioxidant
Sodium carbonate	mineral salt
Sodium carboxymethylcellulose	emulsifier
Sodium citrates	food acid
Sodium dehydroacetate	preservative
Sodium erythorbate	antioxidant
Sodium erythorbin	antioxidant
Sodium ethyl para-hydroxybenzoate	preservative
Sodium ferrocyanide	anti-caking agent
Sodium formate	preservative
Sodium fumarate	food acid
Sodium gluconate	stabilizer
Sodium hydrogen acetate	preservative, acidity regulator
Sodium hydroxide	mineral salt
Sodium lactate	food acid
Sodium malate	food acid
Sodium metabisulfite	preservative, antioxidant, bleaching agent
Sodium methyl para-hydroxybenzoate	preservative
Sodium nitrate	preservative, color fixative
Sodium nitrite	preservative, color fixative
Sodium orthophenyl phenol	preservative
Sodium propionate	preservative
Sodium propyl para-hydroxybenzoate	preservative
Sodium sorbate	preservative
Sodium stearoyl lactylate	emulsifier

Sodium Compound	Use in Food
Sodium succinates	acidity regulator, flavor enhancer
Sodium salts of fatty acids	emulsifier, stabilizer, anti-caking agent
Sodium sulfite	mineral salt, preservative, antioxidant
Sodium sulfite	preservative, antioxidant
Sodium tartrate	food acid
Sodium tetraborate	preservative

The use of so many sodium compounds in prepared and processed foods has alarmed some physicians and nutritionists. They argue that the average person consumes too much sodium from his or her diet. The average person needs only about 500 mg of sodium every day; most people consume more than this—up to 10 times as much. Some studies have implicated increased sodium intake with high blood pressure; newer studies suggest that the link is questionable. However, there has been a push to reduce the amount of sodium most people ingest every day: avoid processed and manufactured foods, read labels on packaged foods (which include an indication of the sodium content), avoid oversalting foods, and use other herbs and spices besides salt in cooking.



Figure **7.2.2**: Food labels include the amount of sodium per serving. This particular label shows that there are 75 mg of sodium in one serving of this particular food item.

Key Takeaways

- Ions form when atoms lose or gain electrons.
- Ionic compounds have positive ions and negative ions.
- Ionic formulas balance the total positive and negative charges.
- Ionic compounds have a simple system of naming.
- Groups of atoms can have an overall charge and make ionic compounds.

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7.3: Writing Formulas for Ionic Compounds

Learning Objectives

- Write the correct formula for an ionic compound.
- Recognize polyatomic ions in chemical formulas.

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 charges to cancel each other out.

Example 7.3.1: Aluminum Nitride and Lithium Oxide

Write the formulas for aluminum nitride and lithium oxide.

Solution

Solution to Example 5.5.1

	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 7.3.2: The Crisscross Method for Lead (IV) Oxide

Write the formula for lead (IV) oxide.

Solution

Solution to Example 5.5.2

Crisscross Method	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 7.3.2

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

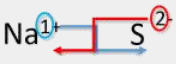
> *Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.*

✓ Example 7.3.3: Sulfur Compound

Write the formula for sodium combined with sulfur.

Solution

Solution to Example 5.5.3

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^{+} 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 subscripts that are 1.	Na_2S

? Exercise 7.3.3

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

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 **7.3.1** lists the most common polyatomic ions.

Table **7.3.1**: Some Polyatomic Ions

Name	Formula
ammonium ion	NH_4^+
acetate ion	$C_2H_3O_2^-$ (also written $CH_3CO_2^-$)
carbonate ion	CO_3^{2-}
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 7.3.4: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

Solution to Example 5.5.4

Crisscross 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 7.3.5

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

Solution

Solution to Example 5.5.5

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 7.3.5

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:

$Al(CH_3COO)_3$

Recognizing Ionic Compounds

There are two ways to recognize ionic compounds.

Method 1

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.

Method 2

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 7.3.6

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. NH_4Cl
d. OF_2

Solution

Solution to Example 5.5.6

Explanation	Answer
a. Sodium is a metal, and oxygen is a nonmetal. Therefore, Na_2O is expected to be ionic via method 1.	Na_2O, ionic
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic via method 1	PCl_3, not ionic
c. The NH_4 in the formula represents the ammonium ion, NH_4^+, which indicates that this compound is ionic via method 2	NH_4Cl, ionic
d. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic via method 1	OF_2, not ionic

Exercise 7.3.6

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Summary

Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

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7.3.1: Ionic Formula Writing

Learning Objectives

- Write formulas for binary ionic compounds
- Relate the Lewis structure to the chemical formula for binary ionic compounds.
- Commit bolded polyatomic formulas to memory.
- Write formulas for ternary (polyatomic) ionic compounds.

Ionic Formulas

Chemical formulas for ionic compounds are called ionic formulas. A proper ionic formula has a cation and an anion in it; an ionic compound is never formed between two cations or two anions only. The key to writing proper ionic formulas is simple: the total positive charge must balance the total negative charge. Because the charges on the ions are characteristic, sometimes we have to have more than one cation or an anion to balance the overall positive and negative charges. It is conventional to use the lowest ratio of ions that are needed to balance the charges.

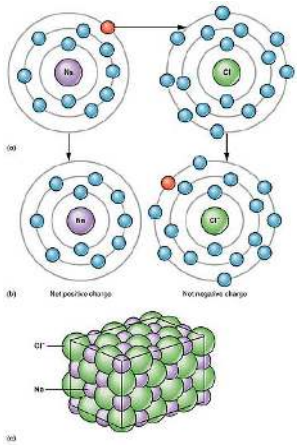


Figure 7.3.1.1: Image taken from: upload.wikimedia.org/wikiped...my_Bonding.JPG

For example, consider the ionic compound between $\mathbf{Na^+}$ and $\mathbf{Cl^-}$. Each ion has a single charge, one positive and one negative, so we need only one ion of each to balance the overall charge. When writing the ionic formula, we follow two additional conventions:

1. write the formula for the cation first and the formula for the anion next, but
2. cross the charges down diagonally.

Thus, for the compound between $\mathbf{Na^+}$ and $\mathbf{Cl^-}$, we have the ionic formula $\mathbf{NaCl}$ (Figure 7.3.1.1). The formula $\mathbf{Na_2Cl_2}$ also has balanced charges, but the convention is to use the lowest ratio of ions, which would be one of each. (Remember from our conventions for writing formulas that we do not write a 1 subscript if there is only one atom of a particular element present.) For the ionic compound between magnesium cations ($\mathbf{Mg^{2+}}$) and oxide anions ($\mathbf{O^{2-}}$, again we need only one of each ion to balance the charges. By convention, the formula is $\mathbf{MgO}$.



Figure 7.3.1.2: NaCl is the formular for Table Salt. The ionic compound NaCl is very common. Red rock salt from the Khewra Salt Mine in Pakistan. (CC BY-SA 4.0; Hubertl).

Rules for Writing Ionic Formulas

Recall ionic compound can be of the following combination: metal/nonmetal or ammonium/nonmetal

1. Recall the cation charge. Superscript this charge to the right of the cation ($Ca^{2+)}$. If metal is multi charged metal (like most transitions and metals below metalloid staircase), then the charge is indicated by a Roman numeral (Lead IV would translate to Pb^{4+}).
2. Recall the anion charge. Superscript this charge to the right of the anion (S^{2-}). If polyatomic ion is present, then put poly in parentheses and superscript charge to the right of this species.
3. Cross charges down diagonally and lose signs. Subscripts that are divisible by the same number must be reduced (ionics are simple compounds). Do not change what is inside a poly. You may keep your parentheses around polyatomic ions.

* Binary compound names will end with ide (except cyanide and hydroxide). This means the anion will come from the periodic table.

** Compounds that contain polyatomic ions will end in ate/ite or the two weird ides (cyanide/hydroxide). You will need to memorize the polyatomic ion table below.**

Example 7.3.1.1:

Write the formulas for the combinations of ions below:

a. Ca^{2+} and Cl^{-}
b. Al^{3+} and F^{-}
c. Li^{+} and O^{2-}

Solution

a. The proper ionic formula is $CaCl_2$.
b. The formula for this compound is AlF_3.
c. After crossing charges diagonally down, the formula will be Li_2O.

? Exercise 7.3.1.2

Write the proper ionic formulas for each of the two given ions.

a. Fe^{2+} and S^{2-}
b. Fe^{3+} and S^{2-}

Answer a

FeS, Subscripts must be reduced for ionic compounds. If this is not done, then the answer will be incorrect.

Answer b

Fe_2S_3, These subscripts cannot be reduced because they are not divisible by the same number.

There also exists a group of ions that contain more than one atom. These are called **polyatomic ions**. Table **7.3.1.1** lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as ***oxyanions***. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge.

Table **7.3.1.1**: Common Polyatomic Ions

Name	Formula and Charge		Name	Formula and Charge
ammonium	$(NH_4)^+$		nitrate	$(NO_3)^-$
acetate	$(C_2H_3O_2)^-$		nitrite	$(NO_2)^-$
bicarbonate (hydrogen carbonate)	$(HCO_3)^-$		carbonate	$(CO_3)^{2-}$
hydroxide	$(OH)^-$		sulfate	$(SO_4)^{2-}$
chlorate	$(ClO_3)^-$		sulfite	$(SO_3)^{2-}$
hypochlorite	$(ClO)^-$		phosphate	$(PO_4)^{3-}$
cyanide	$(CN)^-$		phosphite	$(PO_3)^{3-}$

You will need to commit Table **7.3.1.1** to memory for future tests and quizzes. There are more polyatomic ions than the ones listed in the table above. You will be provided with a list of these additional polyatomic ions for use on tests/quizzes. In our class, this list (List O' Polyatomics) will have the ones you are required to memorize in bold print.

Writing the formulas of ionic compounds has one important difference. If more than one polyatomic ion is needed to balance the overall charge in the formula, enclose the formula of the polyatomic ion in parentheses and write the proper numerical subscript to the right and *outside* the parentheses. Thus, the formula between calcium ions, Ca^{2+}, and nitrate ions, $NO3^-$, is properly written $Ca(NO3)2$, not $CaNO32$ or $CaN2O6$. In our course, I encourage you to keep your polyatomics insides parentheses at all times. Refer back to your rules for writing ionic formulas.

✓ Example 7.3.1.4:

After writing these formulas, watch your instructor teach more examples of this concept by clicking on this link.

a. ammonium sulfide
b. aluminum phosphate
c. iron II phosphite

Solution

a. Ammonium is a polyatomic ion (cation). These species will go first in the formula. Take ammonium $(NH_4)^+$ and combine it with sulfide S^{2-}(ide = periodic table, except for hydroxide/cyanide). While keeping the polyatomic formula within parentheses, cross the ion charges down and lose signs. The resulting formula will be **$(NH_4)_2S$**.

b. Aluminum is Al^{3+} and phosphate is $(PO_4)^{3-}$. While keeping the polyatomic ion inside parentheses, cross charges down and reduce subscripts outside. The final formula for the compound will be **$Al(PO_4)$**. For more advanced chemistry courses, students are encouraged to drop the parentheses if a subscript is not present once charges have been crossed down. I am fine with you always keeping parentheses.

c. Transition metal charges (except for silver and zinc) will always be noted by a Roman numeral. This charge is always positive for the metal ion. Place this charge to the top right corner of the metal atom, Fe^{2+}. Next, recall that phosphite is the polyatomic, $(PO_3)^{3-}$. Cross the charges down diagonally and keep the polyatomic inside the parentheses. The final result will be **$Fe_3(PO_3)_2$**.

? Exercise 7.3.1.4

Write the formulas for the following ionic compounds:

a. ammonium bicarbonate
b. cobalt III nitrite
c. lead IV oxide
d. potassium hydroxide
e. silver phosphide
f. mercury I sulfite

Answer a

$(NH_4)(HCO_3)$, there are no numbers outside the parentheses so you could write NH_4HCO_3 for the answer. Do not combine the hydrogen atoms in the formula.

Answer b

$Co(NO_2)_3$, the parentheses must be kept for this answer.

Answer c

PbO_2, after the charges have been crossed, subscripts must be reduced by the division of common factor

Answer d

$K(OH)$, you could drop ()

Answer e

Ag_3P, phosphide is from the periodic table, not the polyatomic table. Know your endings!!

Answer f

$Hg_2(SO_3)$, you could drop ()

Key Takeaways

- Ions form when atoms lose or gain electrons.
- Ionic compounds have positive ions and negative ions.
- Ionic formulas balance the total positive and negative charges.

Contributors and Attributions

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7.4: Chemical Formulas- How to Represent Compounds

Learning Objectives

- Determine the number of different atoms in a formula.
- Define chemical formula, molecular formula, and empirical formula.

A **chemical formula** is an expression that shows the elements in a compound and the relative proportions of those elements. Water is composed of hydrogen and oxygen in a 2:1 ratio. The chemical formula for water is H_2O. Sulfuric acid is one of the most widely produced chemicals in the United States and is composed of the elements hydrogen, sulfur, and oxygen. The chemical formula for sulfuric acid is H_2SO_4.

Certain groups of atoms are bonded together to form what is called a polyatomic ion that acts as a single unit. Polyatomic ions are discussed in more detail in Section 5.5. Polyatomic ions are enclosed in parenthesis followed by a subscript if more than one of the same ion exist in a chemical formula. The formula $Ca_3(PO_4)_2$ represents a compound with the following:

$$3 \text{ Ca atoms} + 2 \ PO_4^{3-} \text{ ions}$$

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

$$Ca_3(PO_4)_2$$

$$3 \text{ Ca} + 2 \text{ x1 P} + 2 \text{ x 4 O} = 3 \text{ Ca atoms} + 2 \text{ P atoms} + 8 \text{ O atoms}$$

Molecular Formula

A **molecular formula** is a chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound. Ammonia is a compound of nitrogen and hydrogen as shown below:

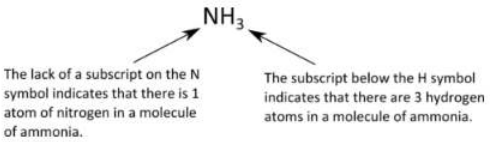


Figure 7.4.1: The molecular formula for ammonia. NH3. There is one atom of nitrogen and 3 atoms of hydrogen in a molecule of ammonia.

Note from the example that there are some standard rules to follow in writing molecular formulas. The arrangements of the elements depend on the particular structure, which is not of concern at this point. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write N_3H for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

Empirical Formula

An **empirical formula** is a formula that shows the elements in a compound in their lowest whole-number ratio. Glucose is an important simple sugar that cells use as their primary source of energy. Its molecular formula is $C_6H_{12}O_6$. Since each of the subscripts is divisible by 6, the empirical formula for glucose is CH_2O. When chemists analyze an unknown compound, often the first step is to determine its empirical formula.

- molecular formula: $C_6H_{12}O_6$
- empirical formula: CH_2O

There are a great many compounds whose molecular and empirical formulas are the same. If the molecular formula cannot be simplified into a smaller whole-number ratio, as in the case of H_2O or P_2O_5, then the empirical formula is also the molecular formula.

Summary

- A chemical formula is an expression that shows the elements in a compound and the relative proportions of those elements.
- If only one atom of a specific type is present, no subscript is used.
- For atoms that have two or more of a specific type of atom present, a subscript is written after the symbol for that atom.
- Polyatomic ions in chemical formulas are enclosed in parentheses followed by a subscript if more than one of the same type of polyatomic ion exist.
- Molecular formulas do not indicate how the atoms are arranged in the molecule.
- The empirical formula tells the lowest whole-number ratio of elements in a compound. The empirical formula does not show the actual number of atoms.

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7.5: Covalent Bonds

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 for another atom to gain one or more electrons. However, some atoms will not 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 form a **covalent bond**.

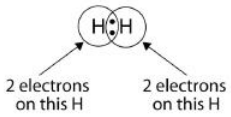
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

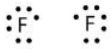
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



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:

H–H

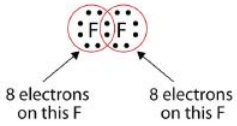
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



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:



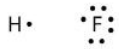
We can also write this using a dash to represent the shared electron pair:



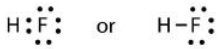
There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F

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:



Note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 7.5.1

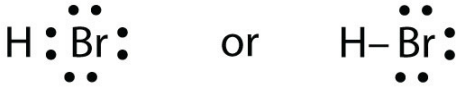
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

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 7.5.1

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

Answer



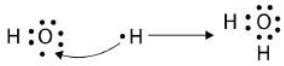
More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Consider H and O atoms:



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. This can be fixed by including a second H atom, whose single electron will make a second covalent bond with the O atom:



(It does not matter what side the second H atom is positioned on.) 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.

Example 7.5.2

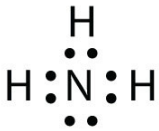
Use a Lewis electron dot diagram to show the covalent bonding in NH_3.

Solution

The N atom has the following Lewis electron dot diagram:



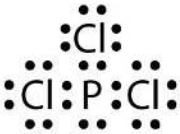
It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:



Exercise 7.5.2

Use a Lewis electron dot diagram to show the covalent bonding in PCl_3.

Answer



There is a simple set of steps for determining the Lewis electron dot diagram of a simple molecule. First, you must identify the central atom and the surrounding atoms. The **central atom** is the atom in the center of the molecule, while the **surrounding atoms** are the atoms making bonds to the central atom. The central atom is usually written first in the formula of the compound (H_2O is the notable exception). After the central and surrounding atoms have been identified, follow these steps:

1. Count the total number of valence electrons. Add extra if the species has negative charges and remove some for every positive charge on the species.
2. Write the central atom and surround it with the surrounding atoms.
3. Put a pair of electrons between the central atom and each surrounding atom.
4. Complete the octets around the surrounding atoms (except for H).
5. Put remaining electrons, if any, around the central atom.
6. Check that every atom has a full valence shell.

Let us try these steps to determine the electron dot diagram for BF_4^-. The B atom is the central atom, and the F atoms are the surrounding atoms. There is a negative sign on the species, so we have an extra electron to consider.

1. **Count the total number of electrons.** B has 3, each F has 7, and there is one extra electron: 3 + 7 + 7 + 7 + 7 + 1 = 32.

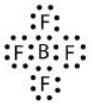
2. **Write the central atom surrounded by surrounding atoms.**



3. **Put a pair of electrons between the central atom and each surrounding atom.** This uses up eight electrons, so we have 32 − 8 = 24 electrons left.



4. **Complete the octets around the surrounding atoms (except for H).** This uses up 24 more electrons, leaving 24 − 24 = 0 electrons left.



5. **Put remaining electrons, if any, around the central atom.** There are no additional electrons to add to the central atom.

6. **Check.** The B atom has eight electrons around it, as does each F atom. Each atom has a complete octet. This is a good Lewis electron dot diagram for BF_4^-.

Sometimes, however, these steps do not work. If we were to follow these steps for the compound formaldehyde (CH_2O), we would get the following:



The H and O atoms have the proper number of electrons, but the C atom only has six electrons around it, not the eight electrons for an octet. How do we fix this?

We fix this by recognizing that two atoms can share more than one pair of electrons. In the case of CH_2O, the O and C atoms share two pairs of electrons, with the following Lewis electron dot diagram as a result:



By circling the electrons around each atom, we can now see that the O and C atoms have octets, while each H atom has two electrons:



Each valence shell is full, so this is an acceptable Lewis electron dot diagram. If we were to use lines to represent the bonds, we would use two lines between the C and O atoms:



The bond between the C and O atoms is a **double bond** and represents two bonding pairs of electrons between the atoms. If the rules for drawing Lewis electron dot diagrams do not work as written, a double bond may be required.

Example 7.5.3: Carbon Dioxide

What is the proper Lewis electron dot diagram for CO_2?

Solution

The central atom is a C atom, with O atoms as surrounding atoms. We have a total of 4 + 6 + 6 = 16 valence electrons. Following the rules for Lewis electron dot diagrams for compounds gives us



The O atoms have complete octets around them, but the C atom only has four electrons around it. The way to solve this dilemma is to make a double bond between carbon and *each* O atom:



Each O atom still has eight electrons around it, but now the C atom also has a complete octet. This is an acceptable Lewis electron dot diagram for CO_2.

Exercise 7.5.3

What is the proper Lewis electron dot diagram for carbonyl sulfide (COS)?

Answer



It is also possible to have a **triple bond,** in which there are three pairs of electrons between two atoms. Good examples of this are elemental nitrogen (N_2) and acetylene (C_2H_2):



Acetylene is an interesting example of a molecule with two central atoms, which are both C atoms. Polyatomic ions are bonded together with covalent bonds. Because they are ions, however, they participate in ionic bonding with other ions. So both major types of bonding can occur at the same time.

Food and Drink Application: Vitamins and Minerals

Vitamins are nutrients that our bodies need in small amounts but cannot synthesize; therefore, they must be obtained from the diet. The word *vitamin* comes from "vital amine" because it was once thought that all these compounds had an amine group (NH_2) in it. This is not actually true, but the name stuck anyway.

All vitamins are covalently bonded molecules. Most of them are commonly named with a letter, although all of them also have formal chemical names. Thus vitamin A is also called retinol, vitamin C is called ascorbic acid, and vitamin E is called tocopherol. There is no single vitamin B; there is a group of substances called the *B complex vitamins* that are all water soluble and participate in cell metabolism. If a diet is lacking in a vitamin, diseases such as scurvy or rickets develop. Luckily, all vitamins are available as supplements, so any dietary deficiency in a vitamin can be easily corrected.

A mineral is any chemical element other than carbon, hydrogen, oxygen, or nitrogen that is needed by the body. Minerals that the body needs in quantity include sodium, potassium, magnesium, calcium, phosphorus, sulfur, and chlorine. Essential minerals that the body needs in tiny quantities (so-called *trace elements*) include manganese, iron, cobalt, nickel, copper, zinc, molybdenum, selenium, and iodine. Minerals are also obtained from the diet. Interestingly, most minerals are consumed in ionic form, rather than as elements or from covalent molecules. Like vitamins, most minerals are available in pill form, so any deficiency can be compensated for by taking supplements.



Supplement Facts

Serving Size 1 Tablet

Each Tablet Contains	% Daily Value
Vitamin A 5000 I.U (50% as Beta Carotene)	100%
Vitamin C 60 mg	100%
Vitamin D 400 I.U.	100%
Vitamin E 30 I.U.	100%
Vitamin K 25 mcg	31%
Thiamin (Vitamin B1) 1.5 mg	100%
Riboflavin (Vitamin B2) 1.7 mg	100%
Niacin 20 mg	100%
Vitamin B6 2 mg	100%
Folic Acid 400 mcg	100%
Vitamin B12 6 mcg	100%
Biotin 30 mcg	10%
Pantothenic Acid 10 mg	100%
Calcium 160 mg	16%
Iron 18 mg	100%
Phosphorus 110 mg	11%
Iodine 150 mcg	100%
Magnesium 100 mg	25%
Zinc 15 mg	100%
Selenium 20 mcg	29%
Copper 2 mg	100%
Manganese 2 mg	100%
Chromium 120 mcg	100%
Molybdenum 75 mcg	100%
Chloride 72 mg	2%
Potassium 80 mg	2%
Boron 150 mcg	*
Nickel 5 mcg	*
Silicon 2 mg	*
Tin 10 mcg	*
Vanadium 10 mcg	*
Lutein 250 mcg	*

* Daily Value (DV) not stablished

Figure 7.5.1: Vitamin and Mineral supplements. Every entry down through pantothenic acid is a vitamin, and everything from calcium and below is a mineral.

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.

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7.5.1: Lewis Electron Dot Structures

Learning Outcomes

- Determine Lewis structure of a compound.

Ionic substances are completely held together by ionic bonds. The full charges of the ions (for example, Na^+ and Cl^- in sodium chloride) cause electrostatic interactions that result in a stable crystal lattice. Ionic compounds exist as extended, orderly arrangements of ions. This is quite different from the structure of molecular substances, which take the form of collections of individual molecules.

The electrons that form a covalent bond are not fully possessed by a single atom (as the electrons in an ion would be) but are shared between the two atoms involved in the bond. The concept of the covalent bond was first proposed in 1916 by the American chemist G. N. Lewis (1875 - 1946), who suggested that sharing electrons was one way that atoms could attain a complete octet of valence electrons. This idea was expanded upon by Linus Pauling (1901 - 1994), who eventually won the Nobel Prize in Chemistry in 1954 for his work on chemical bonding.

Single Covalent Bonds

The simplest covalent bond is formed between two hydrogen atoms. Each hydrogen atom has a single electron, and each needs two electrons for a full outer shell. The hydrogen molecule, H_2, consists of two hydrogen atoms sharing their two valence electrons. Hydrogen can also form covalent bonds with other atoms. For example, hydrogen and chlorine each need one more electron to achieve a noble gas configuration. By sharing valence electrons (each atom donates one), the stable HCl molecule is formed.

We will use a simplified representation of covalent bonds known as **Lewis structures**. These drawings are also know by various other names, including Lewis dot structures or electron dot structures. Each dot in the structure represents one valence electron in the compound. For example, H_2 could be drawn as $H:H$. Each dot represents one valence electron, and the fact that they are placed between the two atoms means that they are being shared bas a covalent bond. For larger molecules, it can become cumbersome to draw out all of the valence electrons, so a bonding pair of electrons can also be drawn as a straight line. Thus, H_2 can also be represented as $H—H$.

If we wanted to show the Lewis structure of HCl, we would draw the following:



We can see that the covalent bond consists of two electrons between the H and the Cl. The H has a full outer shell of two electrons and the chlorine has a full outer shell of eight electrons. Covalent bonds with other halogens can be written the same way.

Similar types of Lewis structures can be written for other molecules that form covalent bonds. Many compounds that contain O, N, C, S, and P are held together by covalent bonds. The number of covalent bonds an atom will form can generally be predicted by the number of electrons an atom requires to fill its valence shell. For example, oxygen has 6 electrons in its outer shell and needs two more to fill this shell, so it will only form two covalent bonds with other atoms. If we look at the water molecule (H_2O) (see figure below), we see that the oxygen atom makes two total bonds (one with each hydrogen atom).

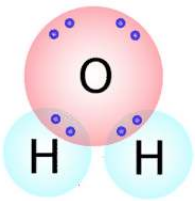
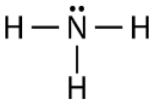


Figure 7.5.1.1: Electron sharing in a water molecule.

As you can see, there are two pairs of electrons not involved in covalent bonding. These unbonded pairs of electrons are known as **lone pairs** and contribute to the overall shape of the molecule. Similarly, nitrogen needs three electrons to complete its valence shell, so it tends to make three covalent bonds, with one lone pair of non-bonding electrons left over.



Again, each of the lines stands for a *pair* of bonding electrons (a single bond), and the lone pair of nitrogen is drawn as two dots.

Double and Triple Bonds

So far we have considered only single bonds, formed by the sharing of one electron from each atom. Many molecules contain **double bonds**, in which each atom shares two electrons, or **triple bonds**, in which each atom shares three electrons. These are represented by drawing two or three lines between the bonded atoms. For example, a carbon-carbon double bond can be written as C :: C or C=C. A carbon-carbon triple bond is shown as C ::: C or with three lines between the two carbon atoms, as seen in the structure of an organic molecule called acetylene (shown in the figure below). Just as N wants to form 3 bonds, other elements tend to form the same number of bonds in different compounds.

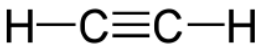
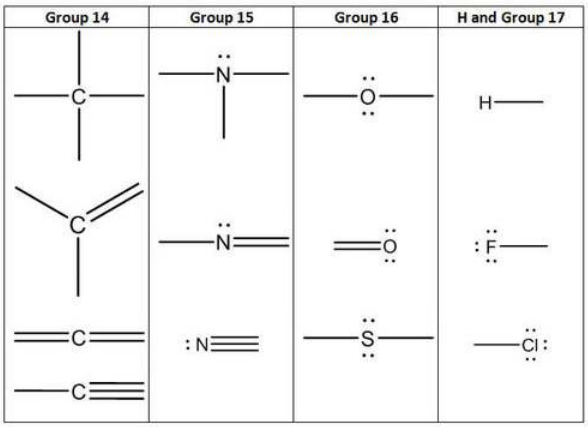


Figure 7.5.1.2: Acetylene molecule.

We will build Lewis structures that satisfy the octet rule to determine how atoms are attached to one another using the components shown in the table below to create structures that follow the octet rule.

Table 7.5.1.1: Components to Build Lewis Structures



Supplemental Resources

Practice drawing Lewis Dot Structures of Covalent Compounds: http://www.wisc-online.com/objects/V...spx?ID=GCH6404

Contributors and Attributions

-
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7.6: Naming Molecular Compounds

Learning Objectives

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

Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substances as water (H_2O) and carbon dioxide (CO_2). These compounds are very different from ionic compounds like sodium chloride ($NaCl$). Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **electrons** in such a way that a **bond** forms between a pair of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

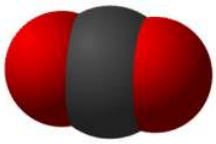


Figure 7.6.1: Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

Larger molecules can have many, many bonds that serve to keep the molecule together. In a large sample of a given molecular compound, all of the individual molecules are identical.

Naming Binary Molecular Compounds

Recall that a molecular formula shows the number of atoms of each element that a molecule contains. A molecule of water contains two hydrogen atoms and one oxygen atom, so its formula is H_2O. A molecule of octane, which is a component of gasoline, contains 8 atoms of carbon and 18 atoms of hydrogen. The molecular formula of octane is C_8H_{18}.



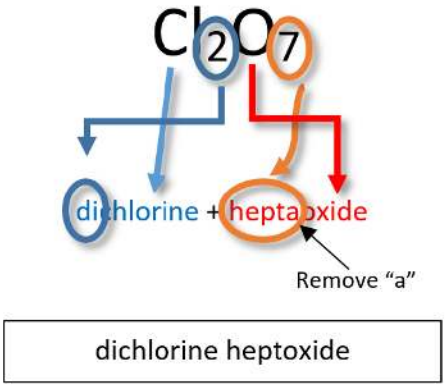
Figure 7.6.2: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

Naming *binary* (two-element) molecular compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 7.6.1 lists these numerical prefixes.

Table 7.6.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

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



Note

- Generally, the less electronegative element is written first in the formula, though there are a few exceptions. Carbon is always first in a formula and hydrogen is after nitrogen in a formula such as NH_3. The order of common nonmetals in binary compound formulas is C, P, N, H, S, I, Br, Cl, O, F.
- The *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms, is tetr**o**xide instead of tetr**ao**xide.
- The prefix is "mono" is not added to the first element's name if there is only one atom of the first element in a molecule.

Some examples of molecular compounds are listed in Table **7.6.2**.

Table **7.6.2**

Formula	Name
NO	nitrogen monoxide
N_2O	dinitrogen monoxide
S_2Cl_2	disulfur dichloride
Cl_2O_7	dichlorine heptoxide

Notice that the *mono-* prefix is not used with the nitrogen in the first compound, but is used with the oxygen in both of the first two examples. The S_2Cl_2 emphasizes that the formulas for molecular compounds are not reduced to their lowest ratios. The *o* of the *mono-* and the *a* of *hepta-* are dropped from the name when paired with oxide.

? Exercise 7.6.1

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

Simple molecular compounds with common names

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

- H_2O: water
- NH_3: ammonia
- CH_4: methane
- H_2O_2: hydrogen peroxide

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system.

Some Compounds Have Both Covalent and Ionic Bonds

If you recall the introduction of polyatomic ions, you will remember that the bonds that hold the polyatomic ions together are covalent bonds. Once the polyatomic ion is constructed with covalent bonds, it reacts with other substances as an ion. The bond between a polyatomic ion and another ion will be ionic. An example of this type of situation is in the compound sodium nitrate. Sodium nitrate is composed of a sodium ion and a nitrate ion. The nitrate ion is held together by covalent bonds and the nitrate ion is attached to the sodium ion by an ionic bond.

Summary

- A molecular compound is usually composed of two or more nonmetal elements.
- Molecular compounds are named with the first element first and then the second element by using the stem of the element name plus the suffix -ide. Numerical prefixes are used to specify the number of atoms in a molecule.

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7.7: Molecules and Chemical Nomenclature

Learning Objectives

- Define *molecule*.
- Name simple molecules based on their formulas.
- Determine a formula of a molecule based on its name.

There are many substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multiatom combinations are called molecules. A molecule is the smallest part of a substance that has the physical and chemical properties of that substance. In some respects, a molecule is similar to an atom. A molecule, however, is composed of more than one atom.

Table **7.7.1**: Elements That Exist as Diatomic Molecules

Hydrogen ($\mathbf{H_2}$)	Oxygen ($\mathbf{O_2}$)	Nitrogen ($\mathbf{N_2}$)	Fluorine ($\mathbf{F_2}$)
Chlorine ($\mathbf{Cl_2}$)	Bromine ($\mathbf{Br_2}$)	Iodine ($\mathbf{I_2}$)	

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules (Table **7.7.1**). As with any molecule, these elements are labeled with a molecular formula, a formal listing of what and how many atoms are in a molecule. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) For example, the molecular formula for elemental hydrogen is H_2, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: O_2, N_2, and so forth. Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, S_8, while phosphorus exists as a four-atom molecule, P_4 (Figure **7.7.1**). Otherwise, we will assume that elements exist as individual atoms, rather than molecules. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

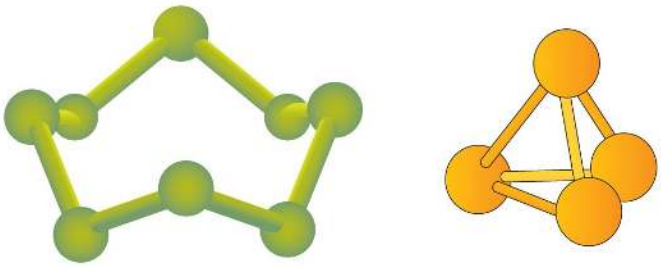


Figure **7.7.1**: Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure **7.7.1** shows two examples of how we will be representing molecules in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a chemical bond and is the connection between two atoms in a molecule.

Many compounds exist as molecules. In particular, when nonmetals connect with other nonmetals, the compounds typically exist as molecules. (Compounds between a metal and a nonmetal are different and will be considered in Section 3.4.) In some cases, there are many different kinds of molecules that can be formed between any given elements, with all the different molecules having different chemical and physical properties. How do we tell them apart?

The answer is a very specific system of naming compounds, called *chemical nomenclature*. By following the rules of nomenclature, each and every compound has its own unique name, and each name refers to one and only one compound. Here, we will start with relatively simple molecules that have only two elements in them, the so-called *binary compounds*:

1. Identify the elements in the molecule from its formula.

2. Begin the name with the element name of the first element. If there is more than one atom of this element in the molecular formula, use a numerical prefix to indicate the number of atoms, as listed in Table **7.7.2**. *Do not use the prefix* mono- *if there is only one atom of the first element.*
3. Name the second element by using three pieces:
   - a numerical prefix indicating the number of atoms of the second element, plus
   - the stem of the element name (e.g., *ox* for oxygen, *chlor* for chlorine, etc.), plus
   - the suffix *-ide*
4. Combine the two words, leaving a space between them.

Table **7.7.2**: Numerical Prefixes Used in Naming Molecular Compounds

The Number of Atoms of an Element	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Let us see how these steps work for a molecule whose molecular formula is SO_2, which has one sulfur atom and two oxygen atoms—this completes step 1. According to step 2, we start with the name of the first element—sulfur. Remember, we do not use the *mono-* prefix for the first element. Now for step 3, we combine the numerical prefix *di-* (see Table **7.7.2**) with the stem *ox-* and the suffix *-ide*, to make *dioxide*. Bringing these two words together, we have the unique name for this compound—sulfur dioxide.

Why all this trouble? There is another common compound consisting of sulfur and oxygen whose molecular formula is SO_3, so the compounds need to be distinguished. SO_3 has three oxygen atoms in it, so it is a different compound with different chemical and physical properties. The system of chemical nomenclature is designed to *give this compound its own unique name*. Its name, if you go through all the steps, is sulfur trioxide. Different compounds have different names.

In some cases, when a prefix ends in *a* or *o;* and the element name begins with *o*, we drop the *a* or *o* on the prefix. So we see *monoxide* or *pentoxide*, rather than *monooxide* or *pentaoxide* in molecule names.

Example 7.7.1

Name each molecule.

a. PF_3
b. CO
c. Se_2Br_2

Solution

a. A molecule with a single phosphorus atom and three fluorine atoms is called phosphorus trifluoride.
b. A compound with one carbon atom and one oxygen atom is properly called carbon monoxide, not carbon monooxide.
c. There are two atoms of each element, selenium and bromine. According to the rules, the proper name here is *diselenium dibromide*.

Exercise 7.7.1

Name each molecule.

a. SF_4
b. P_2S_5

Answer a

sulfur tetrafluoride

Answer b

diphosphorus pentasulfide

One great thing about this system is that it works both ways. From the name of a compound, you should be able to determine its molecular formula. Simply list the element symbols, with a numerical subscript if there is more than one atom of that element, in the order of the name (we do not use the subscript 1 if there is only one atom of the element present; 1 is implied). From the name *nitrogen trichloride*, you should be able to get NCl_3 as the formula for this molecule. From the name *diphosphorus pentoxide*, you should be able to get the formula P_2O_5 (note the numerical prefix on the first element, indicating there is more than one atom of phosphorus in the formula).

Example 7.7.2

Give the formula for each molecule.

a. carbon tetrachloride
b. silicon dioxide
c. trisilicon tetranitride

Solution

a. The name *carbon tetrachloride* implies one carbon atom and four chlorine atoms, so the formula is CCl_4.
b. The name *silicon dioxide* implies one silicon atom and two oxygen atoms, so the formula is SiO_2.
c. We have a name that has numerical prefixes on both elements. *Tri-* means three, and *tetra-* means four, so the formula of this compound is Si_3N_4.

Exercise 7.7.2

Give the formula for each molecule.

a. disulfur difluoride
b. iodine pentabromide

Answer a

S_2F_2

Answer b

IBr_5

Some simple molecules have common names that we use as part of the formal system of chemical nomenclature. For example, H_2O is given the name *water*, not *dihydrogen monoxide*. NH_3 is called *ammonia*, while CH_4 is called *methane*. We will occasionally see other molecules that have common names; we will point them out as they occur.

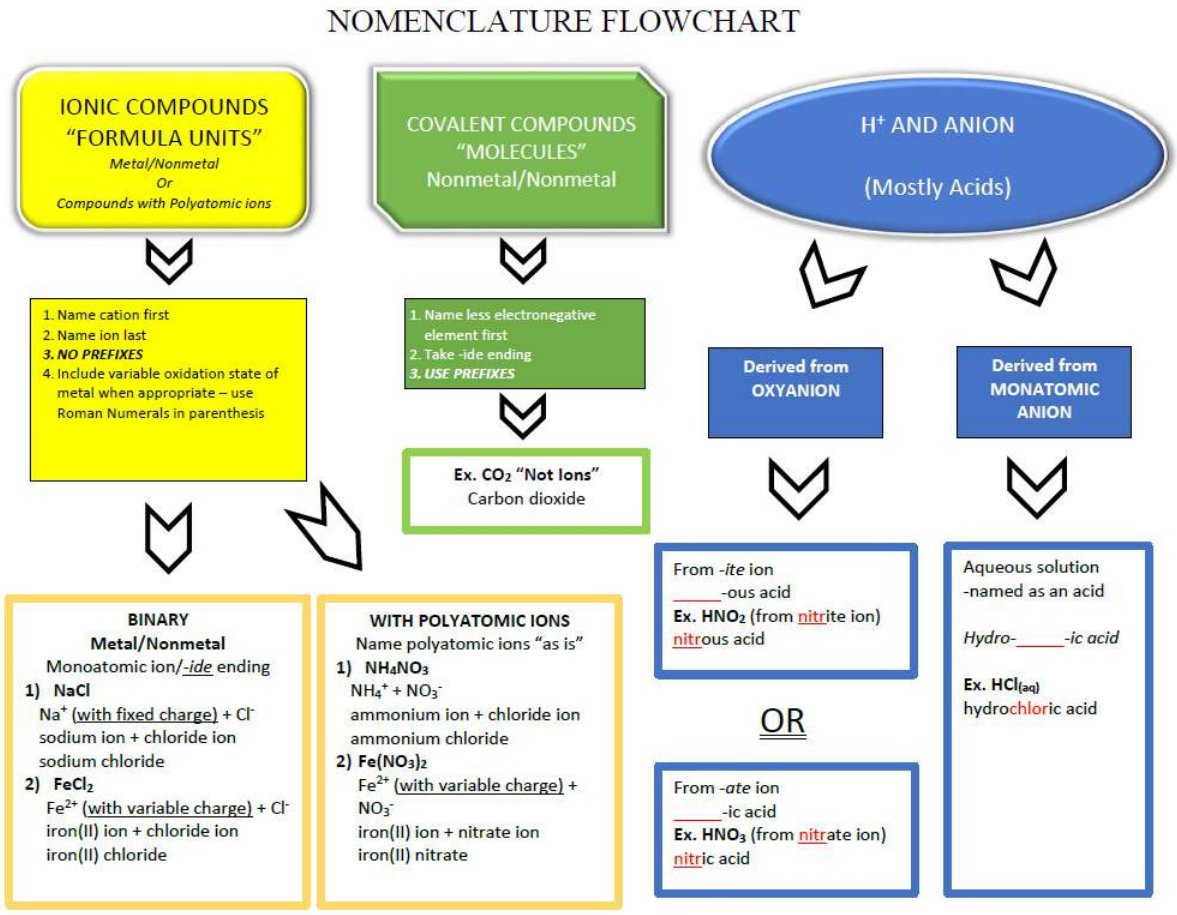
Key Takeaways

- Molecules are groups of atoms that behave as a single unit.
- Some elements exist as molecules: hydrogen, oxygen, sulfur, and so forth.
- There are rules that can express a unique name for any given molecule, and a unique formula for any given name.

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7.8: Nomenclature Summary



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CHAPTER OVERVIEW

8: Organic Chemistry

Photosynthesis involves a whole series of reactions with many chemicals, enzymes, breaking and making chemical bonds, the transfer of electrons and H+ ions, and other chemical processes. The elucidation of the actual steps of photosynthesis-a process still unduplicated artificially-is a major achievement of modern chemistry.

All life on Earth is ultimately based on photosynthesis. Photosynthesis is the process by which plants absorb CO_2 and H_2O from their environment and, in the presence of sunlight, convert those substances into a simple sugar (glucose) and ultimately starches and other building blocks of life. The net photosynthesis chemical reaction is as follows:

$$6CO_2 + 6H_2O \overset{light}{\rightarrow} C_6H_{12}O_6 + 6O_2$$

Oxygen is also a product of photosynthesis. Most forms of animal life (including people) depend on oxygen to breathe, which makes plants indispensable. Virtually all food sources come from plants, eaten either directly (as fruits, vegetables, or grains) or indirectly (as feedstock for meat animals such as cattle, poultry, pigs, sheep, goats, and the like). Plants are absolutely necessary for life to exist.



Figure **8.1**: Photosynthesis. In the presence of the sun, plants perform photosynthesis, the chemical reactions that convert CO_2 and H_2O to glucose. The reaction also produces O_2, which is necessary for animal life. Virtually all life on Earth depends on photosynthesis.

The net reaction for photosynthesis is misleadingly simple. A series of reactions, called light-dependent reactions, start by the absorption of light by pigments (not just chlorophyll, as commonly misunderstood) in plant cells. This is followed by a series of light-independent reactions, so named not because they happen in the dark, but because they do not directly involve light. However, light-independent reactions involve the products of reactions stimulated by light, so they ultimately depend on light. The whole series of reactions involves many chemicals, enzymes, breaking and making chemical bonds, the transfer of electrons and H^+ ions, and other chemical processes. The elucidation of the actual steps of photosynthesis—a process still unduplicated artificially—is a major achievement of modern chemistry.

8.1: Organic Chemistry

8.2: Structures and Names of Alkanes

8.3: Branched-Chain Alkanes

8.4: Condensed Structural and Line-Angle Formulas

8.4.1: IUPAC Nomenclature

8.5: Prelude to Unsaturated and Aromatic Hydrocarbons

8.5.1: Alkenes- Structures and Names

8.5.2: Alkynes

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8.7: Narcotics

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8.1: Organic Chemistry

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate ($AgOCN$) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN$$

However, when heated, ammonium cyanate continues to react and rearranges into urea (NH_2CONH_2), a well-known organic material readily isolated from urine.

$$NH_4OCN \longrightarrow NH_2CONH_2$$

This observation led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory. Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 8.1.1.

Table 8.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane		Inorganic	NaCl
low melting points	−95°C		high melting points	801°C
low boiling points	69°C		high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable		nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds		exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **8.1.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **8.1.1**.

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8.2: Structures and Names of Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure **8.2.1**.

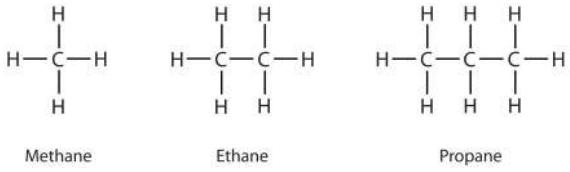


Figure **8.2.1**: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure **8.2.2**).

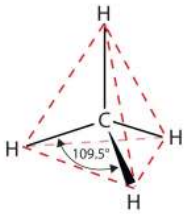


Figure **8.2.2**: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table **8.2.1**.

Table **8.2.1**: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure **8.2.3**. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

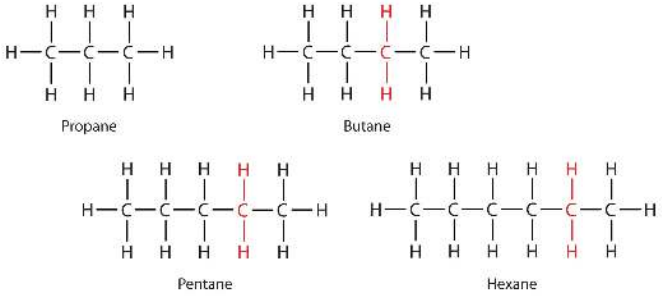


Figure **8.2.3**: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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8.3: Branched-Chain Alkanes

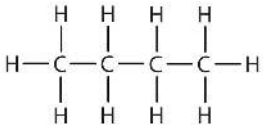
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

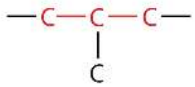
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–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.

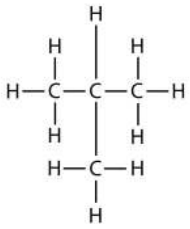


Figure **8.3.1**).

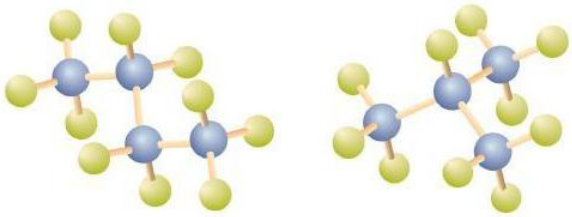
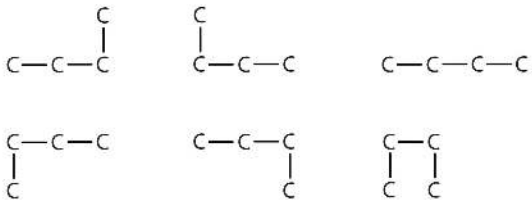


Figure **8.3.1**: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

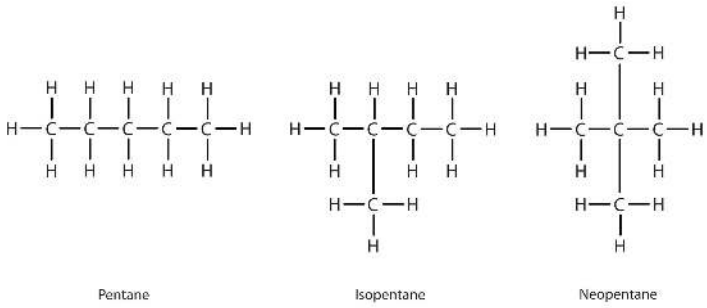
Notice that C_4H_{10} is depicted with a bent chain in Figure **8.3.1**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **8.3.1**.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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8.4: Condensed Structural and Line-Angle Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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8.4.1: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

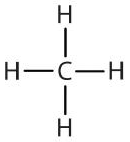
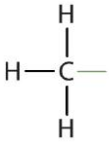
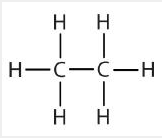
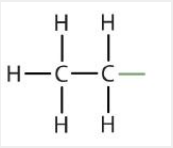
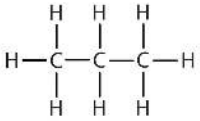
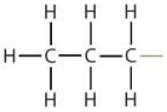
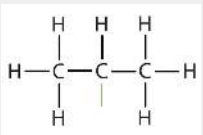
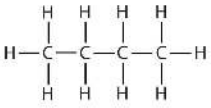
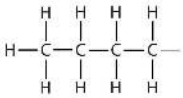
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table **8.4.1.1**) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table **8.4.1.1**: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the -CH_3 group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table **8.4.1.2**. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

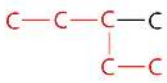
Table **8.4.1.2**: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		$CH_3–$
ethane		ethyl		$CH_3CH_2–$
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl*		$CH_3CH_2CH_2CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example **8.4.1.1**).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

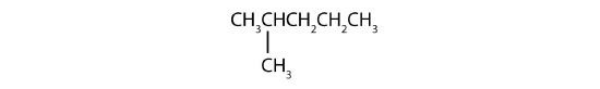
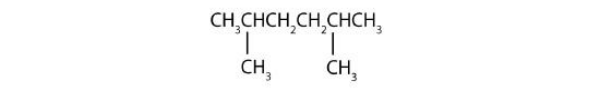
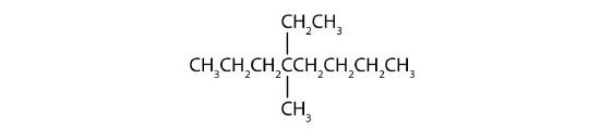


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 8.4.1.1

Name each compound.

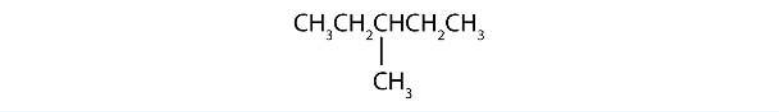
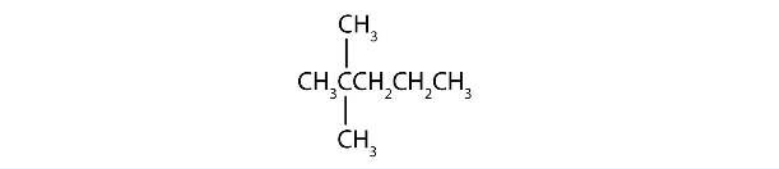
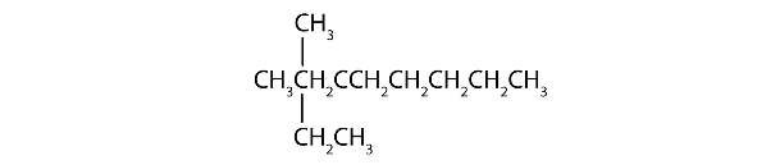
1. 
2. 
3. 

Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexne (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

Exercise 8.4.1.1

Name each compound.

1. 
2. 
3. 

Example 8.4.1.2

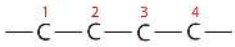
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

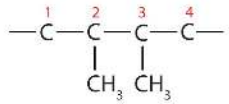
Solution a

In drawing structures, always start with the parent chain.

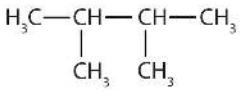
The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.

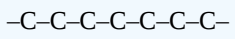


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.

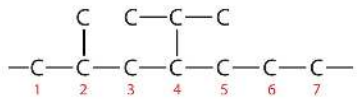


Solution b

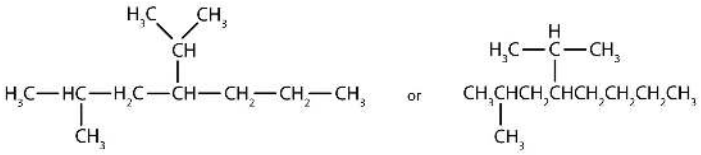
The parent chain is heptane in this case, indicating seven carbon atoms in the LCC.



Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 8.4.1.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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8.5: Prelude to Unsaturated and Aromatic Hydrocarbons

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene).

The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($CHBrClCF_3$).

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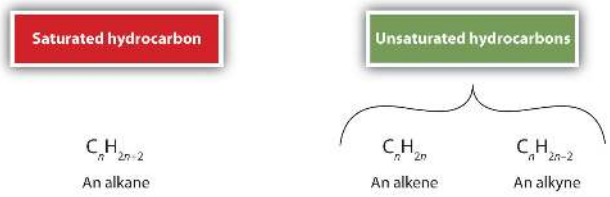
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8.5.1: Alkenes- Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

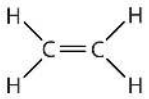


Some representative alkenes—their names, structures, and physical properties—are given in Table **8.5.1.1**.

Table **8.5.1.1**: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table **8.5.1.1**. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table **8.5.1.1**, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure **8.5.1.1**). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

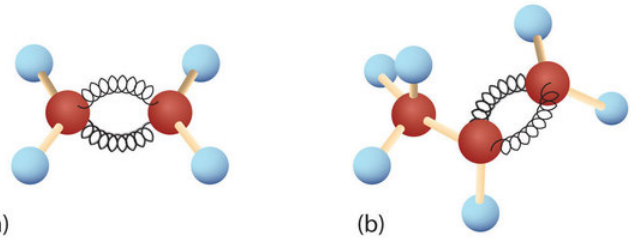
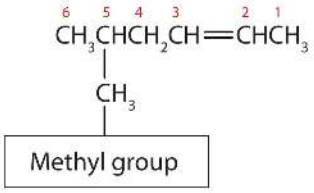


Figure **8.5.1.1**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

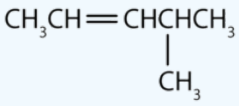
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

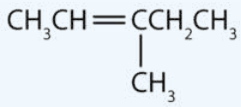
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 8.5.1.1

Name each compound.

a. 

b. 

Solution

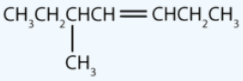
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 8.5.1.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

Example 8.5.1.2

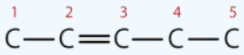
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

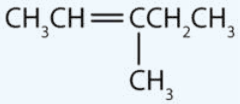
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

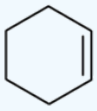


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 8.5.1.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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8.5.2: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure **8.5.2.1**). Its structure is H–C≡C–H.

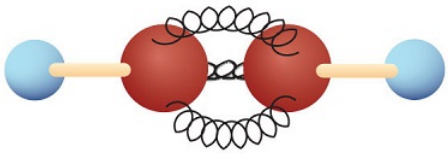


Figure **8.5.2.1**: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

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8.5.3: Aromatic Compounds- Benzene

Learning Objectives

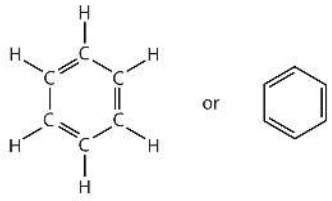
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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8.6: Functional Groups

Learning Outcomes

- Describe the importance and purpose of functional groups in organic reactions.
- Identify and name functional groups in 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 $–CH_2CH_2CH_2CH_3$.

Alkenes and Alkynes

Alkenes are hydrocarbons that contain one or more double bonds between neighboring carbon atoms. Alkynes contain one or more triple bonds between neighboring carbon atoms. The presence of a double or triple bond results in reactivity not present in alkane and alkynes (see figure below) undergo characteristic reactions which will be covered later.



Figure **8.6.1**: Alkenes (left) contain one or more double bonds while alkynes (right) contain one or more triple bonds.

Aromatics

The additional functional group that contains only carbon and hydrogen is an aromatic ring which is a six-carbon ring with alternative double bonds. The aromatic ring is also shown as a ring with a circle in the middle representing the double bonds. Aromatic rings (see figure below) are found in many compounds including steroids and medications.



Figure **8.6.2**: Aromatic rings contain alternating double bonds.

Alcohols

The **alcohol** functional group involves an oxygen atom that is bonded to one hydrogen atom and one carbon atom. The carbon atom will be part of a larger organic structure. One way to indicate a generic alcohol would be with the formula **R–OH**. **R** represents any organic fragment in which a carbon atom is directly bonded to the explicitly indicated functional group (in this case, **OH**). The **R** group is typically a chain of carbon atoms.

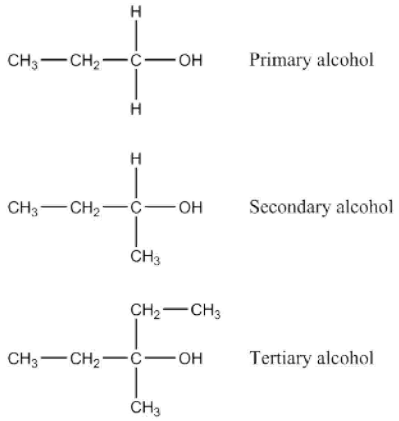


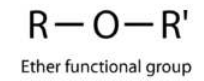
Figure 8.6.3: Primary, secondary, and tertiary alcohols.

Alcohols can be classified as primary, secondary, or tertiary based on the characteristics of the carbon to which it is attached. In a primary alcohol, the carbon bonded directly to the oxygen atom is also bonded to exactly one carbon atom, with the other bonds generally going to hydrogen atoms. In a secondary alcohol, the carbon is attached to two other carbon atoms, and in a tertiary alcohol, the carbon is bonded to three other carbon atoms. The type of alcohol being used will determine the product of certain reactions. Note the naming of alcohols as illustrated in the figure above. The location of the **–OH** group is indicated with the number of the carbon to which it is attached.

We are already familiar with several common alcohols. For example, ethanol (CH_3CH_2OH) is the alcohol present in alcoholic beverages. It is also widely used in the industrial manufacture of other chemicals. Methanol (CH_3OH) is used as a gasoline additive or alternative. Additionally, methanol can be used to manufacture formaldehyde, which is employed in the production of plastics, paints, and other useful substances. Isopropanol is commonly known as rubbing alcohol. In addition to its industrial uses, isopropanol is used to clean various surfaces, including computer monitors, whiteboards, and even skin (e.g., before getting blood drawn).

Ethers

The **ether** functional group consists of an oxygen atom that forms single bonds with two carbon atoms.



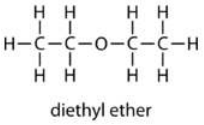


Figure 8.6.4: Ethers

Ethers are good solvents for other organic compounds because of their low reactivity. They readily dissolve nonpolar molecules. Diethyl ether is perhaps the best known ether. It is widely used as a solvent and has been used as an inhalable anesthetic.

Although ethers themselves are relatively unreactive, they can be converted to peroxides after prolonged exposure to oxygen. Peroxides are very reactive and are often explosive at elevated temperatures. Many commercially available ethers come with a small amount of a peroxide scavenger dissolved in them to help prevent this type of safety hazard.

Thiol

The **thiol** functional group contains a sulfur atom bonded to a hydrogen atom. It is very similar to an alcohol functional group with the sulfur replacing the O.

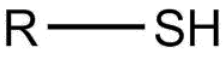


Figure 8.6.5: Thiol

Thiols are also called mercaptans which is derived from the Latin phrase for "capturing mercury" because of the strong bonds it forms with mercury-containing compounds. Some thiol compounds have a distinctive smell similar to rotten eggs. They are often added to natural gas, which itself has no odor, as a way to detect leaks since its odor can be detected by humans in very small amounts. A thiol group is also present in the amino acid cysteine which will be discussed later.

Amines

An **amine** consists of a nitrogen atom bonded to some combination of carbons and hydrogens.

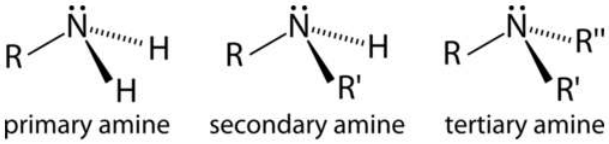


Figure 8.6.6: Amines

Like alcohols, amines can be classified as primary, secondary, or tertiary. However, the rules for assigning these categories are slightly different. In an alcohol, the oxygen atom is always bonded to exactly one carbon atom, so we look at the branching on the adjacent carbon, not the oxygen atom itself. In a neutral amine, the nitrogen can be bonded to one, two, or three carbon atoms, and this is how we decide whether it is called a primary, secondary, or tertiary amine.

Neutral amines are weak bases, because the lone pair on nitrogen can act as a proton acceptor. Many smaller amines have very strong and offensive odors. For example, the aptly-named compounds cadaverine and putrescine are foul-smelling amines, formed as a part of the decay process after death.

Amines serve a wide variety of uses. Diphenylamine acts as a stabilizer for certain types of explosives. Amines are found as components in some lubricating materials, in developers, and are a part of waterproofing textiles. Some amines, such as novocaine, are used as anesthetics. Many pharmaceutical compounds contain amines, including 8 of the 10 most prescribed medications in 2012.

Aldehydes

A very common structural component of organic structures is the **carbonyl**, which is simply a carbon atom and an oxygen atom connected by a double bond. The reactivity of carbonyls is primarily dictated by the polarization of the **C=O** bond, but the surrounding atoms also play a role in its specific reaction pathways. While carbonyl is a component of many functional groups, it is not itself a functional group.

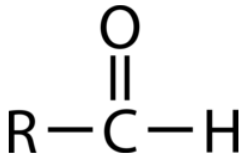


Figure 8.6.7: Aldehyde

An **aldehyde** is a carbonyl in which the carbon atom is bonded to at least one hydrogen atom. The other group attached to the carbonyl may be an **R**-group or a hydrogen atom. Because the hydrogen atom is so small, the partial positive charge on the carbonyl carbon is very easy for other molecules to approach, making aldehydes a particularly reactive type of carbonyl. Aldehydes are versatile reactants for a wide variety of organic syntheses. Many aldehydes also have distinctive flavors and aromas. For example, the flavor of cinnamon is primarily due to the molecule cinnamaldehyde, and vanillin is the aldehyde most responsible for the smell and taste of vanilla extract.

A special aldehyde is the molecule in which the carbonyl is bonded to two hydrogen atoms. This molecule, called formaldehyde, has a wide variety of uses. By itself, it can be used as a tissue preservative or as a very harsh disinfectant. It is also used as a precursor to various materials, including plastics, resins, and other polymers.

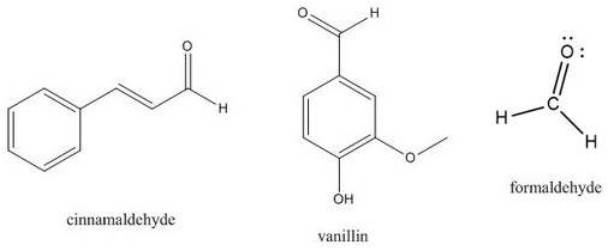


Figure 8.6.8: Examples of molecules with aldehyde functional groups.

Ketones

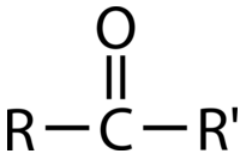


Figure 8.6.9: Ketone

A **ketone** involves a carbonyl in which the carbon atom makes single bonds with two **R**-groups. Ketones undergo most of the same reactions as aldehydes, but they tend to be slightly less reactive. The simplest ketone is acetone, in which the carbonyl carbon is bonded to two CH_3 groups. This ketone is commonly used to remove fingernail polish and serves as an industrial solvent. Methyl ethyl ketone is used as a paint stripper and a solvent. Ketones are also used in the production of various polymers, either as a building block or as a solvent. The **R**-group in a ketone can be the same or different as seen in the example.



Figure 8.6.10: Two examples of ketones.

Carboxylic Acids

Carboxylic acids are another carbonyl-containing functional group, in which the carbon atom is bonded to an **OH** group on one side and either a carbon or hydrogen atom on the other.

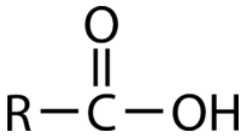


Figure 8.6.11: *Carboxylic acid*

As the name implies, carboxylic acids are weak acids. An **OH** group that is directly connected to a carbonyl will ionize to a small extent when dissolved in water. The reason for this is the relative stability of the resulting anion. A carboxylate ion (see figure below), in which the negative charge is spread over two different oxygen atoms through resonance structures, is more stable than an isolated oxygen-centered anion. The carboxylic acid and carboxylate ion are interchangeable. Carboxylate ions are often present in amino acids.

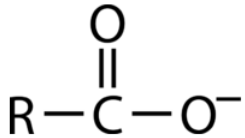


Figure 8.6.12: Carboxylate ion

Carboxylic acids are used in a variety of environments. Formic acid acts as a protective chemical for many stinging insects and plants. Acetic acid gives vinegar its characteristic smell and flavor and is a fundamental biological and industrial building block. Carboxylic acids with longer carbon chains (fatty acids) are used by animals as a way of storing energy and are widely used in the

manufacture of soaps. Some compounds contain multiple carboxylic acids within a single molecule. For example, citric acid (three carboxyl groups) is especially abundant in citrus fruits and it used as a flavoring and preservative in many foods and beverages.

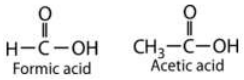


Figure 8.6.13: Carboxylic acids

Esters

An **ester** is similar to a carboxylic acid, in that it contains a carbonyl where the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom. However, the second oxygen atom is bonded to another carbon instead of to an acidic hydrogen atom. Structurally, carboxylic acids and esters are related to one another in the same way as alcohols and ethers.

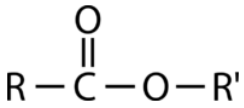


Figure 8.6.14: Ester

Esters can be formed by heating carboxylic acids and alcohols in the presence of an acid catalyst. This process is reversible, and the starting materials can be regenerated by reacting an ester with water in the presence of a weak base.

Some esters have very pleasant odors, so they are used in the manufacture of many perfumes. Propyl acetate contributes to the odor of pears, while isoamyl acetate gives bananas their smell. This ester also serves as an alarm signal for honeybees. Esters are employed in the manufacture of fabrics (polyesters) and Plexiglass. Anesthetics such as procaine and benzocaine also contain esters.

Amides

An **amide** is a carbonyl in which the carbon is attached to one nitrogen atom and one carbon or hydrogen atom. Alternatively, we could define an amide as an amine in which one of the carbon atoms attached to the nitrogen is part of a carbonyl.

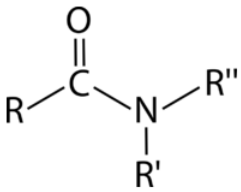


Figure 8.6.15: Amide

An amide can be formed by combining a carboxylic acid and an amine. Only primary and secondary amines can be sued to form amides, since they have a hydrogen that can be replaced with the carbonyl carbon; tertiary amines will not form amides. The amide shown in the figure above was formed from a carboxylic acid and a primary amine.

Amides are used as coloring agents in crayons, pencils, and ink. They are employed in the paper, plastic, and rubber industries. Polyacrylamide is a very widely used amide; it is involved in t he treatment of drinking water and sewage, and in plastics manufacture. The amide Kevlar is widely employed for the production of body armor, and nylon is another type of amide-based polymer.

Haloalkanes

The haloalkanes, also known as alkyl halides, are a group of chemical compounds comprised of an alkane with one or more hydrogens replaced by a halogen atom (Group 17 atom). There is a fairly large distinction between the structural and physical properties of haloalkanes and the structural and physical properties of alkanes. A

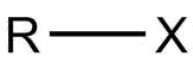


Figure 8.6.16: Amide

Haloalkanes are found in fire extinguishers, refrigerants, propellants, solvents, and medications. They are also a significant source of pollution and their use has been reduced or eliminated in some products. Chlorofluorocarbons (CFCs) were used as refrigerants in air-conditioners but were found to be a major cause of the depletion of the ozone layer. Research and development of alternatives began in the 1970s. Hydrochlorofluorocarbons (HCFCs) have been used for many years since they cause less damage to the ozone layer, but many countries agreed to eliminate HCFCs by 2020.

Contributors and Attributions

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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8.7: Narcotics

Narcotic agents are potent analgesics which are effective for the relief of severe pain. Analgesics are selective central nervous system depressants used to relieve pain. The term analgesic means "without pain". Even in therapeutic doses, narcotic analgesics can cause respiratory depression, nausea, and drowsiness. Long term administration produces tolerance, psychic, and physical dependence called addiction.

Introduction

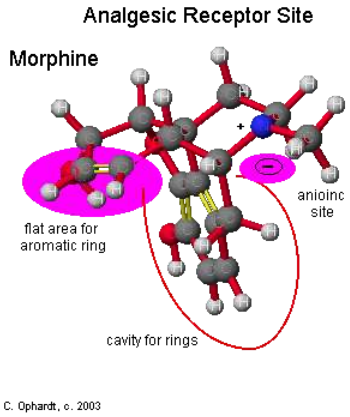
Narcotic agents may be classified into four categories:

1. Morphine and codeine - natural alkaloids of opium.
2. Synthetic derivatives of morphine such as heroin.
3. Synthetic agents which resemble the morphine structure.
4. Narcotic antagonists which are used as antidotes for overdoses of narcotic analgesics.

The main pharmacological action of analgesics is on the cerebrum and medulla of the central nervous system. Another effect is on the smooth muscle and glandular secretions of the respiratory and gastro-intestinal tract. The precise mechanism of action is unknown although the narcotics appear to interact with specific receptor sites to interfere with pain impulses.

Receptor Site

A schematic for an analgesic receptor site may look as shown in the graphic below with morphine. Three areas are needed: a flat areas to accommodate a flat nonpolar aromatic ring, a cavity to accept another series of rings perpendicular, and an anionic site for polar interaction of the amine group.



Enkephalins

Recently investigators have discovered two compounds in the brain called enkephalins which resemble morphine in structure. Each one is a peptide composed of 5 amino acids and differ only in the last amino acid. The peptide sequences are: tyr-gly-gly-phe-leu and tyr-gly-gly-phe-met. Molecular models show that the structures of the enkephalins has some similarities with morphine. The main feature in common appears to be the aromatic ring with the -OH group attached (tyr). Methadone and other similar analgesics have 2 aromatic rings which would be similar to the enkephalins (tyr and phe).

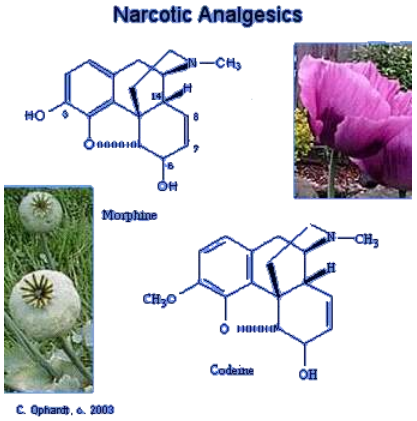
Analgesics may relieve pain by preventing the release of acetylcholine. Enkephalin molecules are released from a nerve cell and bind to analgesic receptor sites on the nerve cell sending the impulse. The binding of enkephalin or morphine-like drugs changes the shape of the nerve sending the impulse in such a fashion as to prevent the cell from releasing acetylcholine. As a result, the pain impulse cannot be transmitted and the brain does not preceive pain.

Morphine and Codeine

Morphine exerts a narcotic action manifested by analgesia, drowsiness, changes in mood, and mental clouding. The major medical action of morphine sought in the CNS is analgesia. Opiates suppress the "cough center" which is also located in the brain stem, the

medulla. Such an action is thought to underlie the use of opiate narcotics as cough suppressants. Codeine appears to be particularly effective in this action and is widely used for this purpose.

Narcotic analgesics cause an addictive physical dependence. If the drug is discontinued, withdrawal symptoms are experienced. Although the reasons for addiction and withdrawal symptoms are not completely known, recent experiments have provided some information. A nucleotide known as cyclicadenosine monophosphate (cAMP) is synthesized with the aid of the enzyme adenylate cyclase. Enkephalin and morphine-like drugs inhibit this enzyme and thus decrease the amount of cAMP in the cells. In order to compensate for the decreased cAMP, the cells synthesize more enzyme in an attempt to produce more cAMP. Since more enzyme has been produced, more morphine is required as an inhibitor to keep the cAMP at a low level. This cycle repeats itself causing an increase in the tolerance level and increasing the amounts of morphine required. If morphine is suddenly withheld, withdrawal symptoms are probably caused by a high concentration of cAMP since the synthesizing enzyme, adenylate cyclase, is no longer being inhibited.



Morphine and codeine are contained in opium from the poppy (*Papaver Somniterum*) plant found in Turkey, Mexico, Southeast Asia, China, and India. This plant is 3-4 feet tall with 5-8 egg shaped capsules on top. Ten days after the poppy blooms in June, incisions are made in the capsules permitting a milky fluid to ooze out. The following day the gummy mass (now brown) is carefully scraped off and pressed into cakes of raw opium to dry.

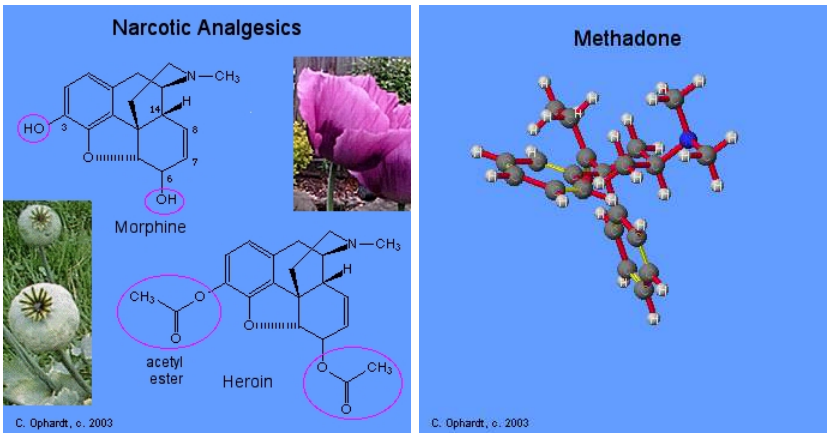
Opium contains over 20 compounds but only morphine (10%) and codeine (0.5%) are of any importance. Morphine is extracted from the opium and isolated in a relatively pure form. Since codeine is in such low concentration, it is synthesized from morphine by an ether-type methylation of an alcohol group. Codeine has only a fraction of the potency compared to morphine. It is used with aspirin and as a cough suppressant.

Heroin

Heroin is synthesized from morphine by a relatively simple esterification reaction of two alcohol (phenol) groups with acetic anhydride (equivalent to acetic acid). Heroin is much more potent than morphine but without the respiratory depression effect. A possible reason may be that heroin passes the blood-brain barrier much more rapidly than morphine. Once in the brain, the heroin is hydrolyzed to morphine which is responsible for its activity.

Synthetic narcotic analgesics include meperidine and methadone. Meperidine is the most common subsitute for morphine. It exerts several pharmacological effects: analgesic, local anesthetic, and mild antihistamine. This multiple activity may be explained by its structural resemblance to morphine, atropine, and histamine.

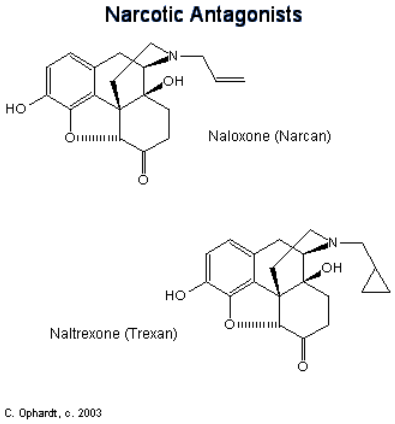
Methadone is more active and more toxic than morphine. It can be used for the relief of may types of pain. In addition it is used as a narcotic substitute in addiction treatment because it prevents morphine abstinence syndrome. Methadone was synthesized by German chemists during Wold War II when the United States and our allies cut off their opium supply. And it is difficult to fight a war without analgesics so the Germans went to work and synthesized a number of medications in use today, including demerol and darvon which is structurally simular to methadone. And before we go further lets clear up another myth. Methadone, or dolophine was not named after Adolf Hitler. The "dol" in dolophine comes from the latin root "dolor." The female name Dolores is derived from it and the term dol is used in pain research to measure pain e.g., one dol is 1 unit of pain.



Even methadone, which looks strikingly different from other opioid agonists, has steric forces which produce a configuration that closely resembles that of other opiates. See the graphic on the left and the top graphic on this page. In other words, steric forces bend the molecule of methadone into the correct configuration to fit into the opiate receptor. When you take methadone it first must be metabolized in the liver to a product that your body can use. Excess methadone is also stored in the liver and blood stream and this is how methadone works its 'time release trick' and last for 24 hours or more. Once in the blood stream metabolized methadone is slowly passed to the brain when it is needed to fill opiate receptors. Methadone is the only effective treatment for heroin addiction. It works to smooth the ups and down of heroin craving and allows the person to function normally.

Narcotic Antagonists

Narcotic Antagonists prevent or abolish excessive respiratory depression caused by the administration of morphine or related compounds. They act by competing for the same analgesic receptor sites. They are structurally related to morphine with the exception of the group attached to nitrogen.



Nalorphine precipitates withdrawal symptoms and produces behavioral disturbances in addition to the antogonism action. Naloxane is a pure antagonist with no morphine like effects. It blocks the euphoric effect of heroin when given before heroin. Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. Naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant

Contributors and Attributions

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CHAPTER OVERVIEW

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9.1: Carbohydrates Fundamentals

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SECTION OVERVIEW

9.1: Carbohydrates Fundamentals

Carbohydrates, also known as sugars, are found in all living organisms. They are essential to the very source of life (ex. Ribose sugars in DNA and RNA) or sustaining life itself (e.g., Metabolic conversion of carbohydrates into usable biochemical energy, ATP). Another important role of carbohydrates is structural (ex. Cellulose in plants). General names for carbohydrates include sugars, starches, saccharides, and polysaccharides. The term saccharide is derived from the Latin word "saccharum" from the sweet taste of sugars. The name "carbohydrate" means a "hydrate of carbon." The name derives from the general formula of carbohydrate is $C_x(H_2O)_y$ - x and y may or may not be equal and range in value from 3 to 12 or more. For example glucose is: $C_6(H_2O)_6$ or is more commonly written, $C_6H_{12}O_6$.

Topic hierarchy

9.1.1: Introduction to Carbohydrates

9.1.2: Carbohydrate Classification

9.1.3: Carbohydrate Isomers

9.1.4: Carbohydrate Overview

9.1.5: Nonreducing Sugar

Template:HideTOC

Thumbnail: Haworth formula of D-glucose.

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9.1.1: Introduction to Carbohydrates

Carbohydrates are the most abundant class of organic compounds found in living organisms. They originate as products of **photosynthesis**, an endothermic reductive condensation of carbon dioxide requiring light energy and the pigment chlorophyll.

$$n\ CO_2 + n\ H_2O + \text{energy} \longrightarrow C_nH_{2n}O_n + n\ O_2$$

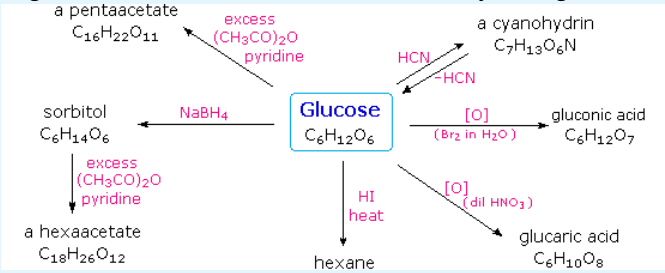
Introduction

The formulas of many carbohydrates can be written as carbon hydrates, $C_n(H_2O)_n$, hence their name. The carbohydrates are a major source of metabolic energy, both for plants and for animals that depend on plants for food. Aside from the sugars and starches that meet this vital nutritional role, carbohydrates also serve as a structural material (cellulose), a component of the energy transport compound ATP, recognition sites on cell surfaces, and one of three essential components of DNA and RNA.

Carbohydrates are called **saccharides** or, if they are relatively small, sugars. Several classifications of carbohydrates have proven

useful, and are outlined in the following table.

1. Carbohydrates have been given non-systematic names, although the suffix **ose** is generally used. The most common carbohydrate is **glucose** ($C_6H_{12}O_6$). Applying the terms defined above, glucose is a monosaccharide, an aldohexose (note that the function and size classifications are combined in one word) and a reducing sugar. The general structure of glucose and many other aldohexoses was established by simple chemical reactions. The following diagram illustrates the kind of evidence considered, although some of the reagents shown here are different from those used by the original scientists.



Glucose and other saccharides are extensively cleaved by periodic acid, thanks to the abundance of vicinal diol moieties in their structure. This oxidative cleavage, known as the **Malaprade reaction** is particularly useful for the analysis of selective O-substituted derivatives of saccharides, since ether functions do not react. The stoichiometry of aldohexose cleavage is shown in the following equation.

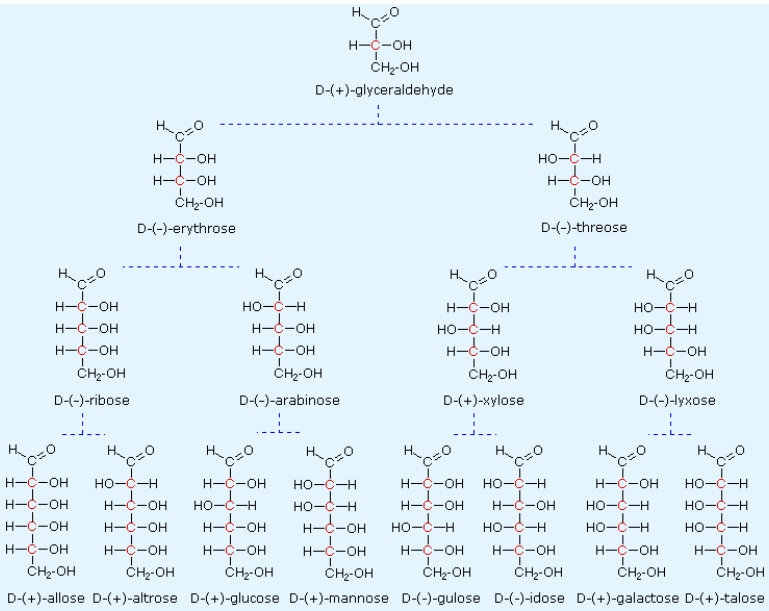
$HOCH_2(CHOH)_4CHO + 5\ HIO_4$	——>	$H_2C{=}O + 5\ HCO_2H + 5\ HIO_3$

The Configuration of Glucose

The four chiral centers in glucose indicate there may be as many as sixteen (2^4) stereoisomers having this constitution. These would exist as eight diastereomeric pairs of enantiomers, and the initial challenge was to determine which of the eight corresponded to glucose. This challenge was accepted and met in 1891 by the German chemist Emil Fischer. His successful negotiation of the stereochemical maze presented by the aldohexoses was a logical tour de force, and it is fitting that he received the 1902 Nobel Prize for chemistry for this accomplishment. One of the first tasks faced by Fischer was to devise a method of representing the configuration of each chiral center in an unambiguous manner. To this end, he invented a simple technique for drawing chains of chiral centers, that we now call the Fischer projection formula. Click on this link for a review.

At the time Fischer undertook the glucose project it was not possible to establish the **absolute configuration** of an enantiomer. Consequently, Fischer made an arbitrary choice for (+)-glucose and established a network of related aldose configurations that he called the **D**-family. The mirror images of these configurations were then designated the **L**-family of aldoses. To illustrate using present day knowledge, Fischer projection formulas and names for the D-aldose family (three to six-carbon atoms) are shown below, with the asymmetric carbon atoms (chiral centers) colored red. The last chiral center in an aldose chain (farthest from the aldehyde group) was chosen by Fischer as the D / L designator site. If the hydroxyl group in the projection formula pointed to the right, it was defined as a member of the D-family. A left directed hydroxyl group (the mirror image) then represented the L-family. Fischer's initial assignment of the D-configuration had a 50:50 chance of being right, but all his subsequent conclusions concerning the relative configurations of various aldoses were soundly based. In 1951 x-ray fluorescence studies of (+)-tartaric acid, carried out in the Netherlands by Johannes Martin Bijvoet (pronounced "buy foot"), proved that Fischer's choice was correct.

It is important to recognize that the sign of a compound's specific rotation (an experimental number) does not correlate with its configuration (D or L). It is a simple matter to measure an optical rotation with a polarimeter. Determining an absolute configuration usually requires chemical interconversion with known compounds by stereospecific reaction paths.



Models of representative aldoses may be examined by clicking on the Fischer formulas for glyceraldehyde, erythrose, threose, ribose, arabinose, allose, altrose, glucose or mannose in the above diagram.

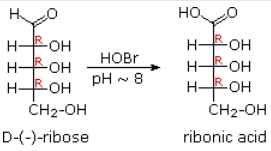
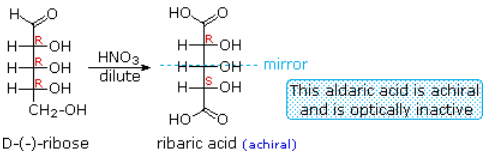
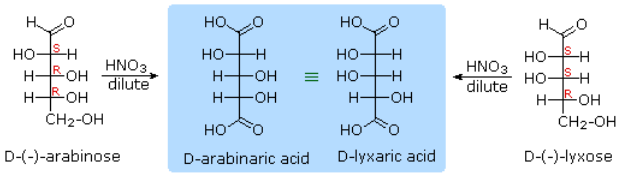
Important Reactions

Emil Fischer made use of several key reactions in the course of his carbohydrate studies. These are described here, together with the information that each delivers.

Oxidation

As noted above, sugars may be classified as **reducing** or **non-reducing** based on their reactivity with Tollens', Benedict's or Fehling's reagents. If a sugar is oxidized by these reagents it is called**reducing**, since the oxidant ($Ag^{(+)}$ or $Cu^{(+2)}$) is reduced in the reaction, as evidenced by formation of a silver mirror or precipitation of cuprous oxide. The Tollens' test is commonly used to detect aldehyde functions; and because of the facile interconversion of ketoses and aldoses under the basic conditions of this test, ketoses such as fructose also react and are classified as reducing sugars.

When the aldehyde function of an aldose is oxidized to a carboxylic acid the product is called an **aldonic acid**. Because of the 2º hydroxyl functions that are also present in these compounds, a mild oxidizing agent such as hypobromite must be used for this conversion (equation 1). If both ends of an aldose chain are oxidized to carboxylic acids the product is called an **aldaric acid**. By converting an aldose to its corresponding aldaric acid derivative, the ends of the chain become identical (this could also be accomplished by reducing the aldehyde to CH_2OH, as noted below). Such an operation will disclose any latent symmetry in the remaining molecule. Thus, ribose, xylose, allose and galactose yield achiral aldaric acids which are, of course, not optically active. The ribose oxidation is shown in equation 2 below.

1.	
2.	
3.	

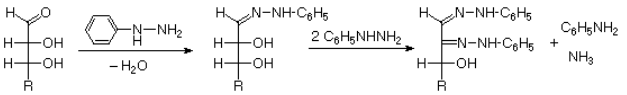
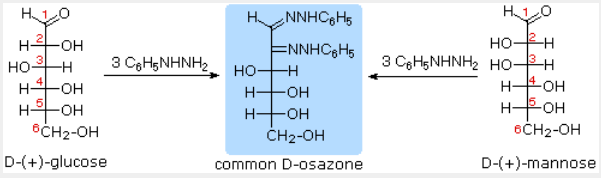
Other aldose sugars may give identical chiral aldaric acid products, implying a unique configurational relationship. The examples of arabinose and lyxose shown in equation 3 above illustrate this result. Remember, a Fischer projection formula may be rotated by 180º in the plane of projection without changing its configuration.

Reduction

Sodium borohydride reduction of an aldose makes the ends of the resulting **alditol** chain identical, $HOCH_2(CHOH)_nCH_2OH$, thereby accomplishing the same configurational change produced by oxidation to an aldaric acid. Thus, allitol and galactitol from reduction of allose and galactose are achiral, and altrose and talose are reduced to the same chiral alditol. A summary of these redox reactions, and derivative nomenclature is given in the following table.

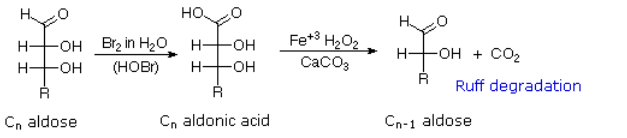
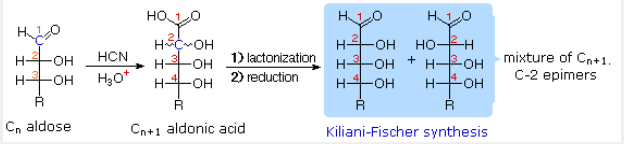
Derivatives of $HOCH_2(CHOH)_nCHO$		
HOBr Oxidation	——>	$HOCH_2(CHOH)_nCO_2H$ an Aldonic Acid
HNO_3 Oxidation	——>	$H_2OC(CHOH)_nCO_2H$ an Aldaric Acid
$NaBH_4$ Reduction	——>	$HOCH_2(CHOH)_nCH_2OH$ an Alditol

Osazone Formation

1.	
2.	

The osazone reaction was developed and used by Emil Fischer to identify aldose sugars differing in configuration only at the alpha-carbon. The upper equation shows the general form of the osazone reaction, which effects an alpha-carbon oxidation with formation of a bis-phenylhydrazone, known as an osazone. Application of the osazone reaction to D-glucose and D-mannose demonstrates that these compounds differ in configuration only at C-2.

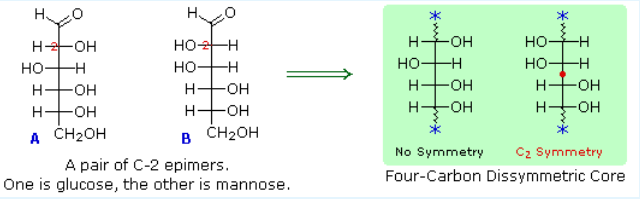
Chain Shortening and Lengthening

1.	
2.	

These two procedures permit an aldose of a given size to be related to homologous smaller and larger aldoses. The importance of these relationships may be seen in the array of aldose structurespresented earlier, where the structural connections are given by the dashed blue lines. Thus Ruff degradation of the pentose arabinose gives the tetrose erythrose. Working in the opposite direction, a Kiliani-Fischer synthesis applied to arabinose gives a mixture of glucose and mannose. An alternative chain shortening procedure known as the Wohl degradation is essentially the reverse of the Kiliani-Fischer synthesis.

Using these reactions we can now follow Fischer's train of logic in assigning the configuration of D-glucose.

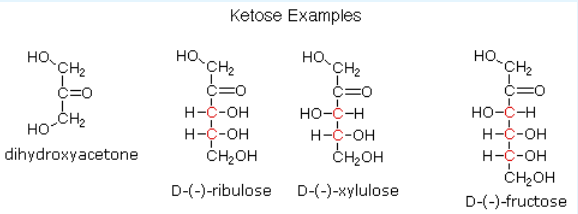
1. In order to determine which of these epimers was glucose, Fischer made use of the inherent C_2 symmetry in the four-carbon dissymmetric core of one epimer (**B**). This is shown in the following diagram by a red dot where the symmetry axis passes through the projection formula. Because of this symmetry, if the aldehyde and 1°-alcohol functions at the ends of the chain are exchanged, epimer **B** would be unchanged; whereas **A** would be converted to a different compound. By clicking on the diagram, the consequences of such an exchange will be displayed.



Ketoses

If a monosaccharide has a carbonyl function on one of the inner atoms of the carbon chain it is classified as a **ketose**. Dihydroxyacetone may not be a sugar, but it is included as the ketose analog of glyceraldehyde. The carbonyl group is commonly found at C-2, as illustrated by the following examples (chiral centers are colored red). As expected, the carbonyl function of a ketose may be reduced by sodium borohydride, usually to a mixture of epimeric products. D-Fructose, the sweetest of the common natural sugars, is for example reduced to a mixture of D-glucitol (sorbitol) and D-mannitol, named after the aldohexoses from which they may also be obtained by analogous reduction. Mannitol is itself a common natural carbohydrate.

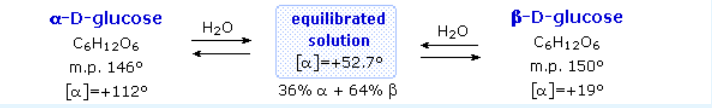
Although the ketoses are distinct isomers of the aldose monosaccharides, the chemistry of both classes is linked due to their facile interconversion in the presence of acid or base catalysts. This interconversion, and the corresponding epimerization at sites alpha to the carbonyl functions, occurs by way of an **enediol** tautomeric intermediate. By clicking on the diagram, an equation illustrating these isomerizations will be displayed.



Because of base-catalyzed isomerizations of this kind, the Tollens' reagent is not useful for distinguishing aldoses from ketoses or for specific oxidation of aldoses to the corresponding aldonic acids. Oxidation by HOBr is preferred for the latter conversion.

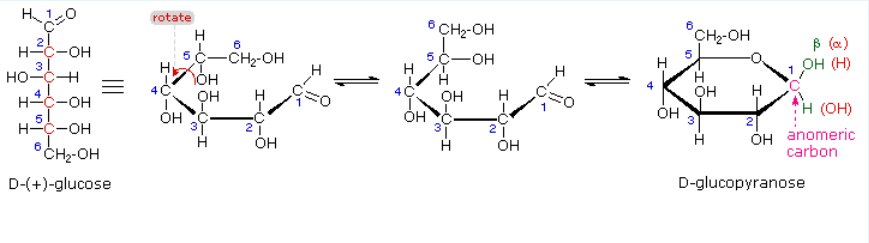
Anomeric Forms of Glucose

Fischer's brilliant elucidation of the configuration of glucose did not remove all uncertainty concerning its structure. Two different crystalline forms of glucose were reported in 1895. Each of these gave all the characteristic reactions of glucose, and when dissolved in water equilibrated to the same mixture. This equilibration takes place over a period of many minutes, and the change in optical activity that occurs is called **mutarotation**. These facts are summarized in the diagram below.



When glucose was converted to its pentamethyl ether (reaction with excess CH_3I & AgOH), two different isomers were isolated, and neither exhibited the expected aldehyde reactions. Acid-catalyzed hydrolysis of the pentamethyl ether derivatives, however, gave a tetramethyl derivative that was oxidized by Tollen's reagent and reduced by sodium borohydride, as expected for an aldehyde. These reactions will be displayed above by clicking on the diagram.

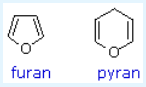
The search for scientific truth often proceeds in stages, and the structural elucidation of glucose serves as a good example. It should be clear from the new evidence presented above, that the open chain pentahydroxyhexanal structure drawn above must be modified. Somehow a new stereogenic center must be created, and the aldehyde must be deactivated in the pentamethyl derivative. A simple solution to this dilemma is achieved by converting the open aldehyde structure for glucose into a cyclic hemiacetal, called a **glucopyranose**, as shown in the following diagram. The linear aldehyde is tipped on its side, and rotation about the C4-C5 bond brings the C5-hydroxyl function close to the aldehyde carbon. For ease of viewing, the six-membered hemiacetal structure is drawn as a flat hexagon, but it actually assumes a chair conformation. The hemiacetal carbon atom (C-1) becomes a new stereogenic center, commonly referred to as the **anomeric carbon**, and the α and β-isomers are called **anomers**.



We can now consider how this modification of the glucose structure accounts for the puzzling facts noted above. First, we know that hemiacetals are in equilibrium with their carbonyl and alcohol components when in solution. Consequently, fresh solutions of either alpha or beta-glucose crystals in water should establish an equilibrium mixture of both anomers, plus the open chain chain form. This will be shown above by clicking on the diagram. Note that despite the very low concentration of the open chain aldehyde in this mixture, typical chemical reactions of aldehydes take place rapidly.

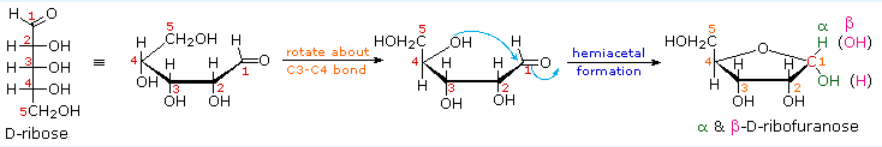
Second, a pentamethyl ether derivative of the pyranose structure converts the hemiacetal function to an acetal. Acetals are stable to base, so this product should not react with Tollen's reagent or be reduced by sodium borohydride. Acid hydrolysis of acetals regenerates the carbonyl and alcohol components, and in the case of the glucose derivative this will be a tetramethyl ether of the pyranose hemiacetal. This compound will, of course, undergo typical aldehyde reactions. By clicking on the diagram a second time this relationship will be displayed above.

5. Cyclic Forms of Monosaccharides

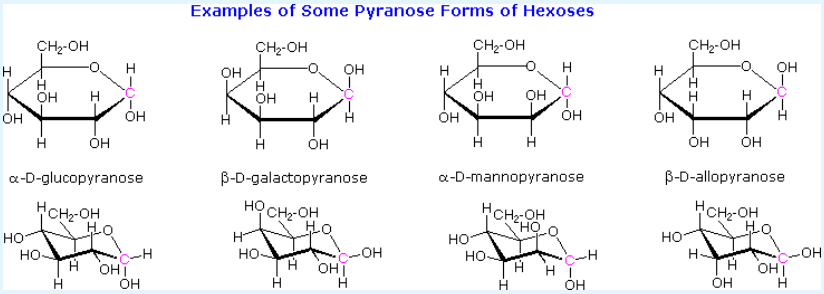


As noted above, the preferred structural form of many monosaccharides may be that of a cyclic hemiacetal. Five and six-membered rings are favored over other ring sizes because of their low angle and eclipsing strain. Cyclic structures of this kind are termed **furanose** (five-membered) or **pyranose** (six-membered), reflecting the ring size relationship to the common heterocyclic compounds furan and pyran shown on the right. Ribose, an important aldopentose, commonly adopts a furanose structure, as shown in the following illustration. By convention for the D-family, the five-membered furanose ring is drawn in an edgewise projection with the ring oxygen positioned away from the viewer. The anomeric carbon atom (colored red here) is placed on the right. **The upper bond to this carbon is defined as beta, the lower bond then is alpha**.

Click on the following diagram to see a model of β-D-ribofuranose.



The cyclic pyranose forms of various monosaccharides are often drawn in a flat projection known as a **Haworth formula**, after the British chemist, Norman Haworth. As with the furanose ring, the anomeric carbon is placed on the right with the ring oxygen to the back of the edgewise view. In the D-family, the alpha and beta bonds have the same orientation defined for the furanose ring (beta is up & alpha is down). These Haworth formulas are convenient for displaying stereochemical relationships, but do not represent the true shape of the molecules. We know that these molecules are actually puckered in a fashion we call a chair conformation. Examples of four typical pyranose structures are shown below, both as Haworth projections and as the more representative chair conformers. The anomeric carbons are colored red.



Models of these glucose, galactose, mannose and allose pyranose structures may be viewed by Clicking Here.

A practice page for examining the configurations of aldohexoses may be viewed by Clicking Here.

The size of the cyclic hemiacetal ring adopted by a given sugar is not constant, but may vary with substituents and other structural features. Aldolhexoses usually form pyranose rings and their pentose homologs tend to prefer the furanose form, but there are many counter examples. The formation of acetal derivatives illustrates how subtle changes may alter this selectivity. By clicking on the above diagram. the display will change to illustrate this. A pyranose structure for D-glucose is drawn in the rose-shaded box on the left. Acetal derivatives have been prepared by acid-catalyzed reactions with benzaldehyde and acetone. As a rule, benzaldehyde forms

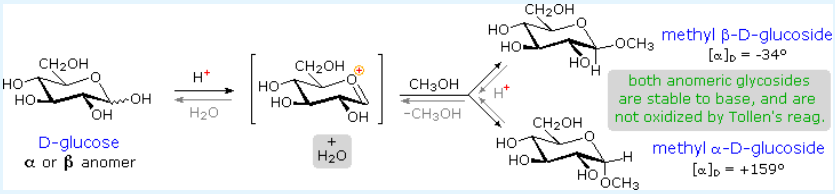
six-membered cyclic acetals, whereas acetone prefers to form five-membered acetals. The top equation shows the formation and some reactions of the 4,6-O-benzylidene acetal, a commonly employed protective group. A methyl glycoside derivative of this compound (see below) leaves the C-2 and C-3 hydroxyl groups exposed to reactions such as the periodic acid cleavage, shown as the last step. The formation of an isopropylidene acetal at C-1 and C-2, center structure, leaves the C-3 hydroxyl as the only unprotected function. Selective oxidation to a ketone is then possible. Finally, direct di-O-isopropylidene derivatization of glucose by reaction with excess acetone results in a change to a furanose structure in which the C-3 hydroxyl is again unprotected. However, the same reaction with D-galactose, shown in the blue-shaded box, produces a pyranose product in which the C-6 hydroxyl is unprotected. Both derivatives do not react with Tollens' reagent. This difference in behavior is attributed to the cis-orientation of the C-3 and C-4 hydroxyl groups in galactose, which permits formation of a less strained five-membered cyclic acetal, compared with the trans-C-3 and C-4 hydroxyl groups in glucose. Derivatizations of this kind permit selective reactions to be conducted at different locations in these highly functionalized molecules.

The ring size of these cyclic monosaccharides was determined by oxidation and chain cleavage of their tetra methyl ether derivatives. To see how this was done for glucose Click Here.

6. Glycosides

Acetal derivatives formed when a monosaccharide reacts with an alcohol in the presence of an acid catalyst are called **glycosides**. This reaction is illustrated for glucose and methanol in the diagram below. In naming of glycosides, the "ose" suffix of the sugar name is replaced by "oside", and the alcohol group name is placed first. As is generally true for most acetals, glycoside formation involves the loss of an equivalent of water. The diether product is stable to base and alkaline oxidants such as Tollen's reagent. Since acid-catalyzed aldolization is reversible, glycosides may be hydrolyzed back to their alcohol and sugar components by aqueous acid.

The anomeric methyl glucosides are formed in an equilibrium ratio of 66% alpha to 34% beta. From the structures in the previous diagram, we see that pyranose rings prefer chair conformations in which the largest number of substituents are equatorial. In the case of glucose, the substituents on the beta-anomer are all equatorial, whereas the C-1 substituent in the alpha-anomer changes to axial. Since substituents on cyclohexane rings prefer an equatorial location over axial (methoxycyclohexane is 75% equatorial), the preference for alpha-glycopyranoside formation is unexpected, and is referred to as the **anomeric effect**.



Glycosides abound in biological systems. By attaching a sugar moiety to a lipid or benzenoid structure, the solubility and other properties of the compound may be changed substantially. Because of the important modifying influence of such derivatization, numerous enzyme systems, known as glycosidases, have evolved for the attachment and removal of sugars from alcohols, phenols and amines. Chemists refer to the sugar component of natural glycosides as the **glycon** and the alcohol component as the **aglycon**. Two examples of naturally occurring glycosides and one example of an amino derivative will be displayed above by clicking on the diagram. Salicin, one of the oldest herbal remedies known, was the model for the synthetic analgesic aspirin. A large class of hydroxylated, aromatic oxonium cations called **anthocyanins** provide the red, purple and blue colors of many flowers, fruits and some vegetables. Peonin is one example of this class of natural pigments, which exhibit a pronounced pH color dependence. The oxonium moiety is only stable in acidic environments, and the color changes or disappears when base is added. The complex changes that occur when wine is fermented and stored are in part associated with glycosides of anthocyanins. Finally, amino derivatives of ribose, such as cytidine play important roles in biological phosphorylating agents, coenzymes and information transport and storage materials.

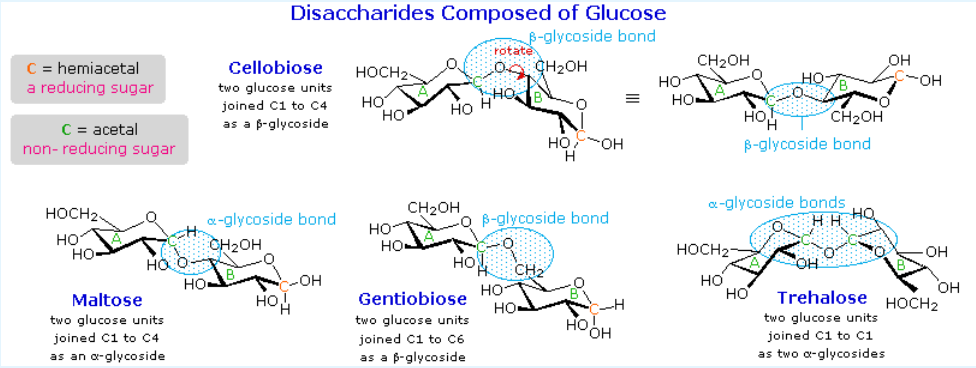
For a discussion of the anomeric effect Click Here. For examples of structurally and functionally modified sugars Click Here.

Disaccharides

When the alcohol component of a glycoside is provided by a hydroxyl function on another monosaccharide, the compound is called a **disaccharide**. Four examples of disaccharides composed of two glucose units are shown in the following diagram. The individual glucopyranose rings are labeled A and B, and the glycoside bonding is circled in light blue. Notice that the glycoside bond may be alpha, as in maltose and trehalose, or beta as in cellobiose and gentiobiose. Acid-catalyzed hydrolysis of these disaccharides yields glucose as the only product. Enzyme-catalyzed hydrolysis is selective for a specific glycoside bond, so an alpha-glycosidase cleaves maltose and trehalose to glucose, but does not cleave cellobiose or gentiobiose. A beta-glycosidase has the opposite activity.

In order to draw a representative structure for cellobiose, one of the glucopyranose rings must be rotated by 180º, but this feature is often omitted in favor of retaining the usual perspective for the individual rings. The bonding between the glucopyranose rings in cellobiose and maltose is from the anomeric carbon in ring A to the C-4 hydroxyl group on ring B. This leaves the anomeric carbon in

ring B free, so cellobiose and maltose both may assume alpha and beta anomers at that site (the beta form is shown in the diagram). Gentiobiose has a beta-glycoside link, originating at C-1 in ring A and terminating at C-6 in ring B. Its alpha-anomer is drawn in the diagram. Because cellobiose, maltose and gentiobiose are hemiacetals they are all reducing sugars (oxidized by Tollen's reagent). Trehalose, a disaccharide found in certain mushrooms, is a bis-acetal, and is therefore a non-reducing sugar. A systematic nomenclature for disaccharides exists, but as the following examples illustrate, these are often lengthy.



Disaccharides made up of other sugars are known, but glucose is often one of the components. Two important examples of such mixed disaccharides will be displayed above by clicking on the diagram. Lactose, also known as milk sugar, is a galactose-glucose compound joined as a beta-glycoside. It is a reducing sugar because of the hemiacetal function remaining in the glucose moiety. Many adults, particularly those from regions where milk is not a dietary staple, have a metabolic intolerance for lactose. Infants have a digestive enzyme which cleaves the beta-glycoside bond in lactose, but production of this enzyme stops with weaning. Cheese is less subject to the lactose intolerance problem, since most of the lactose is removed with the whey. Sucrose, or cane sugar, is our most commonly used sweetening agent. It is a non-reducing disaccharide composed of glucose and fructose joined at the anomeric carbon of each by glycoside bonds (one alpha and one beta). In the formula shown here the fructose ring has been rotated 180º from its conventional perspective.

To examine a model of sucrose Click Here

Additional Topics

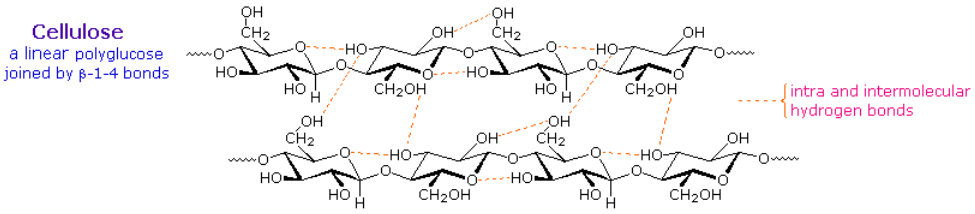
For a brief discussion of sweetening agents Click Here. For examples of some larger saccharide oligomers Click Here.

Polysaccharides

As the name implies, polysaccharides are large high-molecular weight molecules constructed by joining monosaccharide units together by glycosidic bonds. They are sometimes called **glycans**. The most important compounds in this class, cellulose, starch and glycogen are all polymers of glucose. This is easily demonstrated by acid-catalyzed hydrolysis to the monosaccharide. Since partial hydrolysis of cellulose gives varying amounts of cellobiose, we conclude the glucose units in this macromolecule are joined by beta-glycoside bonds between C-1 and C-4 sites of adjacent sugars. Partial hydrolysis of starch and glycogen produces the disaccharide maltose together with low molecular weight dextrans, polysaccharides in which glucose molecules are joined by alpha-glycoside links between C-1 and C-6, as well as the alpha C-1 to C-4 links found in maltose. Polysaccharides built from other monosaccharides (e.g. mannose, galactose, xylose and arabinose) are also known, but will not be discussed here.

Over half of the total organic carbon in the earth's biosphere is in **cellulose**. Cotton fibers are essentially pure cellulose, and the wood of bushes and trees is about 50% cellulose. As a polymer of glucose, cellulose has the formula $(C_6H_{10}O_5)_n$ where n ranges from 500 to 5,000, depending on the source of the polymer. The glucose units in cellulose are linked in a linear fashion, as shown in the drawing below. The beta-glycoside bonds permit these chains to stretch out, and this conformation is stabilized by intramolecular hydrogen bonds. A parallel orientation of adjacent chains is also favored by intermolecular hydrogen bonds. Although an individual hydrogen bond is relatively weak, many such bonds acting together can impart great stability to certain conformations of large molecules. Most animals cannot digest cellulose as a food, and in the diets of humans this part of our vegetable intake functions as roughage and is eliminated largely unchanged. Some animals (the cow and termites, for example) harbor intestinal microorganisms that breakdown cellulose into monosaccharide nutrients by the use of beta-glycosidase enzymes.

Cellulose is commonly accompanied by a lower molecular weight, branched, amorphous polymer called **hemicellulose**. In contrast to cellulose, hemicellulose is structurally weak and is easily hydrolyzed by dilute acid or base. Also, many enzymes catalyze its hydrolysis. Hemicelluloses are composed of many D-pentose sugars, with xylose being the major component. Mannose and mannuronic acid are often present, as well as galactose and galacturonic acid.



Starch is a polymer of glucose, found in roots, rhizomes, seeds, stems, tubers and corms of plants, as microscopic granules having characteristic shapes and sizes. Most animals, including humans, depend on these plant starches for nourishment. The structure of starch is more complex than that of cellulose. The intact granules are insoluble in cold water, but grinding or swelling them in warm water causes them to burst.

The released starch consists of two fractions. About 20% is a water soluble material called **amylose**. Molecules of amylose are linear chains of several thousand glucose units joined by alpha C-1 to C-4 glycoside bonds. Amylose solutions are actually dispersions of hydrated helical micelles. The majority of the starch is a much higher molecular weight substance, consisting of nearly a million glucose units, and called **amylopectin**. Molecules of amylopectin are branched networks built from C-1 to C-4 and C-1 to C-6 glycoside links, and are essentially water insoluble. Representative structural formulas for amylose and amylopectin will be shown above by clicking on the diagram. To see an expanded structure for amylopectin click again on the diagram. The branching in this diagram is exaggerated, since on average, branches only occur every twenty five glucose units.

Hydrolysis of starch, usually by enzymatic reactions, produces a syrupy liquid consisting largely of glucose. When cornstarch is the feedstock, this product is known as **corn syrup**. It is widely used to soften texture, add volume, prohibit crystallization and enhance the flavor of foods.

Glycogen is the glucose storage polymer used by animals. It has a structure similar to amylopectin, but is even more highly branched (about every tenth glucose unit). The degree of branching in these polysaccharides may be measured by enzymatic or chemical analysis.

For examples of chemical analysis of branching Click Here.

Synthetic Modification of Cellulose

Cotton, probably the most useful natural fiber, is nearly pure cellulose. The manufacture of textiles from cotton involves physical manipulation of the raw material by carding, combing and spinning selected fibers. For fabrics the best cotton has long fibers, and short fibers or cotton dust are removed. Crude cellulose is also available from wood pulp by dissolving the lignan matrix surrounding it. These less desirable cellulose sources are widely used for making paper.

In order to expand the ways in which cellulose can be put to practical use, chemists have devised techniques for preparing solutions of cellulose derivatives that can be spun into fibers, spread into a film or cast in various solid forms. A key factor in these transformations are the three free hydroxyl groups on each glucose unit in the cellulose chain, --$[C_6H_7O(OH)_3]_n$--. Esterification of these functions leads to polymeric products having very different properties compared with cellulose itself.

Cellulose Nitrate, first prepared over 150 years ago by treating cellulose with nitric acid, is the earliest synthetic polymer to see general use. The fully nitrated compound, --$[C_6H_7O(ONO_2)_3]_n$--, called guncotton, is explosively flammable and is a component of smokeless powder. Partially nitrated cellulose is called **pyroxylin**. Pyroxylin is soluble in ether and at one time was used for photographic film and lacquers. The high flammability of pyroxylin caused many tragic cinema fires during its period of use. Furthermore, slow hydrolysis of pyroxylin yields nitric acid, a process that contributes to the deterioration of early motion picture films in storage.

Cellulose Acetate, --$[C_6H_7O(OAc)_3]_n$--, is less flammable than pyroxylin, and has replaced it in most applications. It is prepared by reaction of cellulose with acetic anhydride and an acid catalyst. The properties of the product vary with the degree of acetylation. Some chain shortening occurs unavoidably in the preparations. An acetone solution of cellulose acetate may be forced through a spinneret to generate filaments, called **acetate rayon**, that can be woven into fabrics.

Viscose Rayon, is prepared by formation of an alkali soluble xanthate derivative that can be spun into a fiber that reforms the cellulose polymer by acid quenching. The following general equation illustrates these transformations. The product fiber is called **viscose rayon**.

ROH	$\xrightleftharpoons{NaOH}$	$RO^{(-)}\ Na^{(+)}$ + S=C=S	$\longrightarrow$	RO-$CS_2^{(-)}\ Na^{(+)}$	$\xrightarrow{H_3O^{(+)}}$	ROH
cellulose				viscose solution		rayon

Contributors

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9.1.2: Carbohydrate Classification

There are a variety of interrelated classification schemes. The most useful classification scheme divides the carbohydrates into groups according to the number of individual simple sugar units. **Monosaccharides** contain a single unit; **disaccharides** contain two sugar units; and **polysaccharides** contain many sugar units as in polymers - most contain glucose as the monosaccharide unit.

Monosaccharides	**Disaccharides**

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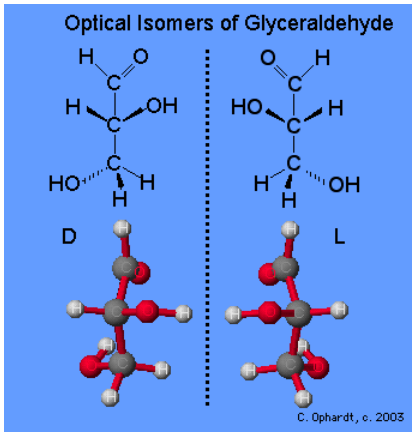
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9.1.3: Carbohydrate Isomers

Glyceraldehyde, the simplest carbohydrate, exhibits properties of a chiral or optical isomer compound. This molecule forms the basis for the designation of the isomers of all of the carbohydrates.

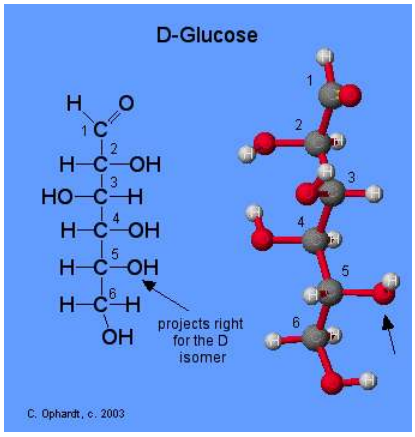
Introduction

Glyceraldehyde can exist in two isomeric forms that are mirror images of each other which are shown below. The absolute configuration is defined by the molecule on the far left as the D-glyceraldehyde. With the aldehyde group in the "up" direction, the the -OH group must project to the right side of the molecule for the D isomer. Chemists have used this configuration of D-glyceraldehyde to determine the optical isomer families of the rest of the carbohydrates. All naturally occurring monosaccharides belong to the D optical family. It is remarkable that the chemistry and enzymes of all living things can tell the difference between the geometry of one optical isomer over the other.



Monosaccharides are assigned to the D-family according to the projection of the -OH group to the **right** on the chiral carbon that is the farthest from the carbonyl (aldehyde) group. This is on carbon # 5 if the carbonyl carbon is # 1.

Note: For whatever reason, the ball and stick model does not completely match the projections of the -OH groups on carbons # 2 and 4. It is in the way that the flat Fischer model has been defined.



How many chiral carbons can you find? List them. If necessary Review Chiral Compounds to find the definitions.Then check the answer from the drop down menu.

Answer

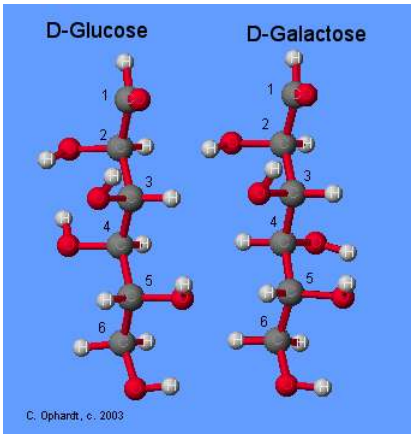
Compare Glucose and Galactose

Examine the structures of glucose and galactose carefully. Which -OH group determines that they both are the D isomer? Then check the answer from the drop down menu.

Answer

Isomers have different arrangements of atoms. Which carbon bonding to -OH and -H is different in glucose vs. galactose? This single difference makes glucose and galactose isomers. Then check the answer from the drop down menu.

Answer



Contributors

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9.1.4: Carbohydrate Overview

Introduction

The chemistry of carbohydrates most closely resembles that of alcohol, aldehyde, and ketone functional groups. As a result, the modern definition of a CARBOHYDRATE is that the compounds are polyhydroxy aldehydes or ketones. The chemistry of carbohydrates is complicated by the fact that there is a functional group (alcohol) on almost every carbon. In addition, the carbohydrate may exist in either a straight chain or a ring structure. Ring structures incorporate two additional functional groups: the hemiacetal and acetal.

A major part of the carbon cycle occurs as carbon dioxide is converted to carbohydrates through photosynthesis. Carbohydrates are utilized by animals and humans in metabolism to produce energy and other compounds.

Photosynthesis is a complex series of reactions carried out by algae, phytoplankton, and the leaves in plants, which utilize the energy from the sun. The simplified version of this chemical reaction is to utilize carbon dioxide molecules from the air and water molecules and the energy from the sun to produce a simple sugar such as glucose and oxygen molecules as a by product. The simple sugars are then converted into other molecules such as starch, fats, proteins, enzymes, and DNA/RNA i.e. all of the other molecules in living plants. All of the "matter/stuff" of a plant ultimately is produced as a result of this photosynthesis reaction.

Di- and Poly-Carbohydrates

- **Monosaccharides** contain one sugar unit such as glucose, galactose, fructose, etc.
- **Disaccharides** contain two sugar units. In almost all cases one of the sugars is glucose, with the other sugar being galactose, fructose, or another glucose. Common disaccharides are maltose, lactose, and sucrose.
- **Polysaccharides** contain many sugar units in long polymer chains of many repeating units. The most common sugar unit is glucose. Common poly saccharides are starch, glycogen, and cellulose.

Table 1: Common Carbohydrates

Name	Derivation of name and Source
Monosaccharides	
Glucose	From Greek word for sweet wine; grape sugar, blood sugar, dextrose.
Galactose	Greek word for milk--"galact", found as a component of lactose in milk.
Fructose	Latin word for fruit--"fructus", also known as levulose,found in fruits and honey; sweetest sugar.
Ribose	Ribose and Deoxyribose are found in the backbone structure of RNA and DNA, respectively.
Disaccharides - contain two monosaccharides	
Sucrose	French word for sugar--"sucre", a disaccharide containing glucose and fructose; table sugar, cane sugar, beet sugar.
Lactose	Latin word for milk--"lact"; a disaccharide found in milk containing glucose and galactose.
Maltose	French word for "malt"; a disaccharide containing two units of glucose; found in germinating grains, used to make beer.
Common Polysaccharides	
Starch	Plants store glucose as the polysaccharide starch. The cereal grains (wheat, rice, corn, oats, barley) as well as tubers such as potatoes are rich in starch.
Cellulose	The major component in the rigid cell walls in plants is cellulose and is a linear polysaccharide polymer with many glucose monosaccharide units.
Glycogen	This is the storage form of glucose in animals and humans which is analogous to the starch in plants. Glycogen is synthesized and stored mainly in the liver and the muscles.

Metabolism

Metabolism occurs in animals and humans after the ingestion of organic plant or animal foods. In the cells a series of complex reactions occurs with oxygen to convert for example glucose sugar into the products of carbon dioxide and water and ENERGY. This reaction is also carried out by bacteria in the decomposition/decay of waste materials on land and in the water.

Combustion occurs when any organic material is reacted (burned) in the presence of oxygen to give off the products of carbon dioxide and water and ENERGY. The organic material can be any fossil fuel such as natural gas (methane), oil, or coal. Other organic materials that combust are wood, paper, plastics, and cloth.

The whole purpose of both processes is to convert chemical energy into other forms of energy such as heat.

Contributors

- Charles Ophardt, Professor Emeritus, Elmhurst College; Virtual Chembook

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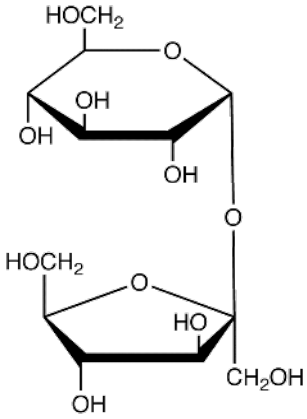
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9.1.5: Nonreducing Sugar

A nonreducing sugar is a carbohydrate that is not oxidized by a weak oxidizing agent (an oxidizing agent that oxidizes aldehydes but not alcohols, such as the Tollen's reagent) in basic aqueous solution. The characteristic property of nonreducing sugars is that, in basic aqueous medium, they do not generate any compounds containing an aldehyde group.

eg: sucrose, which contains neither a hemiacetal group nor a hemiketal group and, therefore, is stable in water.



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9.2: Lipids

On July 11, 2003, the Food and Drug Administration amended its food labeling regulations to require that manufacturers list the amount of *trans* fatty acids on Nutrition Facts labels of foods and dietary supplements, effective January 1, 2006. This amendment was a response to published studies demonstrating a link between the consumption of *trans* fatty acids and an increased risk of heart disease. *Trans* fatty acids are produced in the conversion of liquid oils to solid fats, as in the creation of many commercial margarines and shortenings. They have been shown to increase the levels of low-density lipoproteins (LDLs)—complexes that are often referred to as bad cholesterol—in the blood. In this chapter, you will learn about fatty acids and what is meant by a *trans* fatty acid, as well as the difference between fats and oils. You will also learn what cholesterol is and why it is an important molecule in the human body.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure 9.2.1 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.

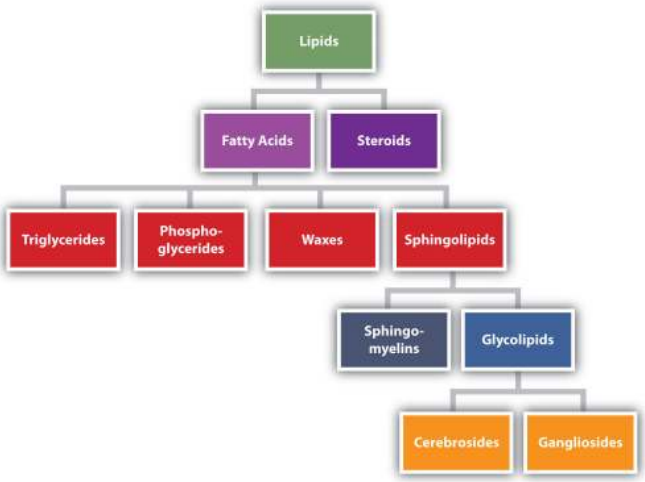


Figure 9.2.1: Lipid Organization Based on Structural Relationships

Lipid categorized into fatty acids and steroids. Fatty acids are further separated into triglycerides, phospho-glycerides, waxes, and sphingolipids. Sphingolipids are separated into sphingo-myelins and glycolipids. Glycolipids are separated into cerebrosides and gangliosides.

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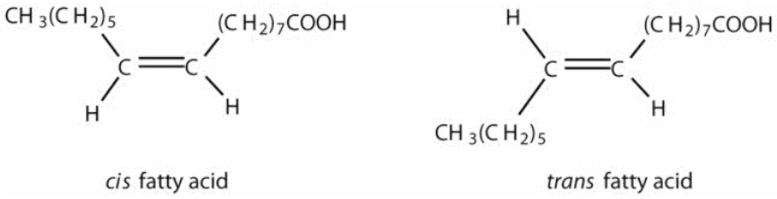
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9.2.1: Fatty Acids

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table **9.2.1.1** lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table **9.2.1.1**: Some Common Fatty Acids Found in Natural Fats

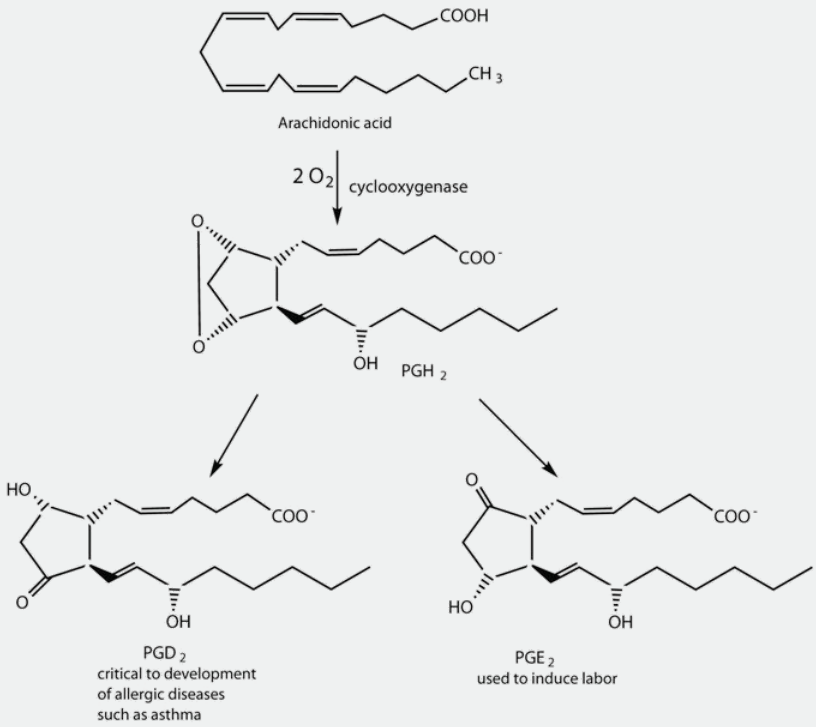
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	olive oil
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	−5	canola oil
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	−11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$	−50	liver

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.



Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of PGE_2 are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure **9.2.1.2*a***). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure **9.2.1.2*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.

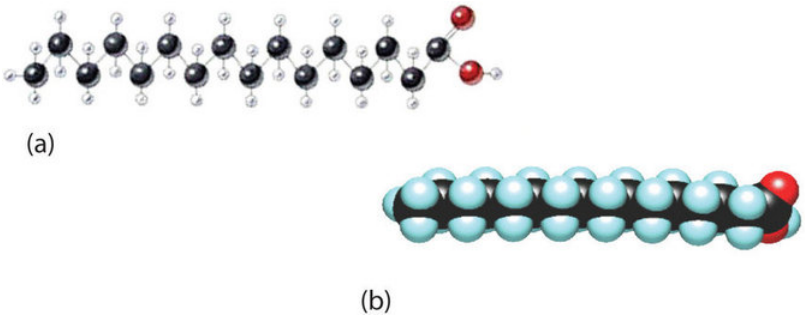
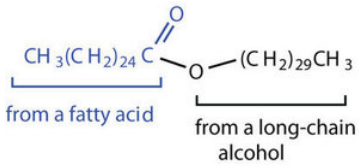


Figure **9.2.1.2**: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Myricyl cerotate
(found in carnauba wax)

Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

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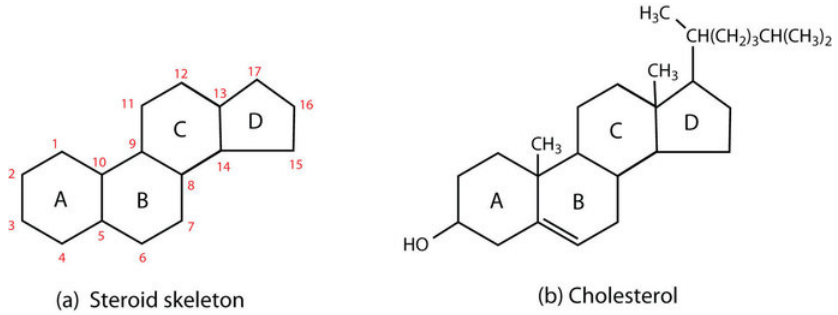
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9.2.2: Steroids

Learning Objectives

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).



(a) Steroid skeleton (b) Cholesterol

Figure 9.2.2.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure **9.2.2.1*a***. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure **9.2.2.1*b***) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure **9.2.2.2**). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



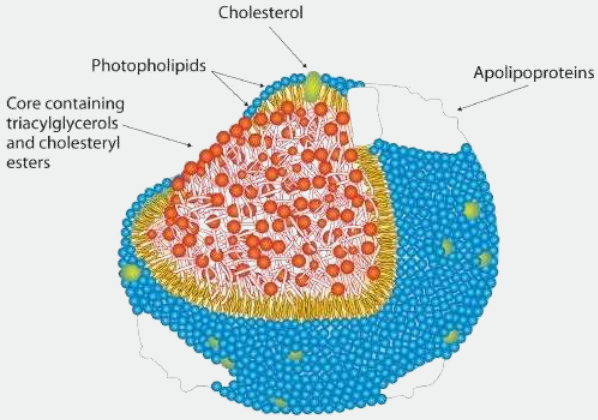
Figure **9.2.2.2**: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.



Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

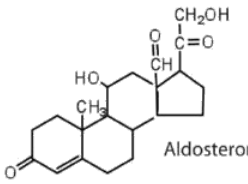
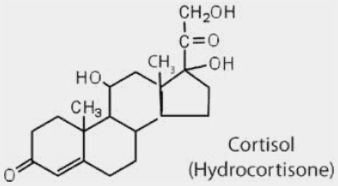
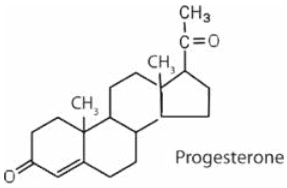
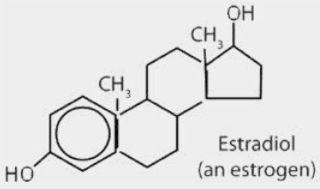
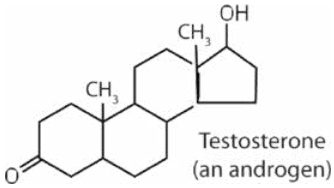
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

Steroid Hormones

Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

The adrenocortical hormones, such as aldosterone and cortisol (Table **9.2.2.1**), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table **9.2.2.1**: Representative Steroid Hormones and Their Physiological Effects

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle
 Testosterone (an androgen)	stimulates and maintains male sex characteristics

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex

hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure **9.2.2.3**) and an amine such as the amino acid glycine (part (b) of Figure **9.2.2.3**). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

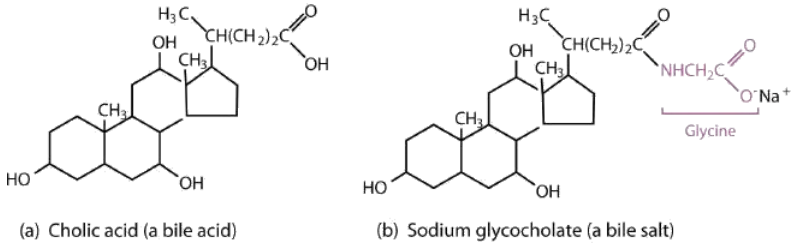


Figure **9.2.2.3** Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

Because they contain both hydrophobic and hydrophilic groups, bile salts are highly effective detergents and emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

> Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver's bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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9.3: Amino Acids

Athletics are very competitive these days at all levels, from school sports to the pros. Everybody is looking for that edge that will make them faster, stronger, and more physically fit. One approach taken by many athletes is the use of amino acid supplements. The theory is that the increase in amino acids in the diet will lead to increased protein for muscles. However, the only real benefit comes to the people who make and sell the pills. Studies have not shown any advantage obtained by the athletes themselves; they are better off just maintaining a healthy diet.

Amino Acids

An **amino acid** is a compound that contains both an amine group ($-NH_2$) and a carboxyl group ($-COOH$) in the same molecule. While any number of amino acids can be imagined, biochemists generally reserve the term for a group of 20 amino acids which are formed and used by living organisms. The figure below shows the general structure of an amino acid.

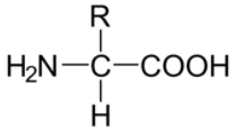


Figure **9.3.1**: An amino acid is an organic molecule that contains an amine group, a carboxyl group, and a side chain (**R**), all bonded to a central carbon atom.

The amino acid and carboxyl group of an amino acid are both covalently bonded to a central carbon atom. That carbon atom is also bonded to a hydrogen atom and an **R** group. It is this **R** group which varies from one amino acid to another and is called the amino acid side chain.

The nature of the side chains accounts for the variability in physical and chemical properties of the different amino acids. Some side chains consist of nonpolar aliphatic or aromatic hydrocarbons. Other side chains are polar, while some are acidic or basic.

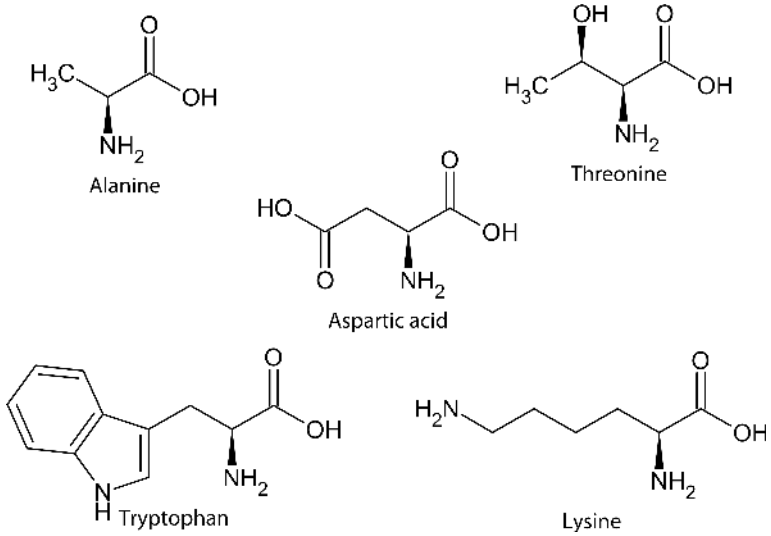


Figure **9.3.2**: Five of the twenty biologically relevant amino acids, each having a distinct side chain (**R**). Alanine's side chain is nonpolar, while threonine's is polar. Tryptophan is one of several amino acids whose side chain is aromatic. Aspartic acid has an acidic side chain, while lysine has a basic side chain.

The table below lists the names of the 20 naturally occurring amino acids along with a three-letter abbreviation which is used to describe sequences of linked amino acids.

Table **9.3.1**: Amino acids and Abbreviations

Amino Acid	Abbreviation	Amino Acid	Abbreviation
Alanine	Ala	Leucine	Leu
Arginine	Arg	Lysine	Lys
Asparagine	Asp	Methionine	Met
Aspartic acid	Asp	Phenylalanine	Phe
Cysteine	Cys	Proline	Pro
Glutamine	Gln	Serine	Ser
Glutamic acid	Glu	Threonine	Thr
Glycine	Gly	Tryptophan	Trp
Histidine	His	Tyrosine	Tyr
Isoleucine	Ile	Valine	Val

Another more recent set of abbreviations employs only one letter. Leucine would be designated by L, serine by S, tyrosine by Y. The advantage of this system comes when listing the amino acid sequence of a protein that may contain over 100 amino acids in its chain.

Summary

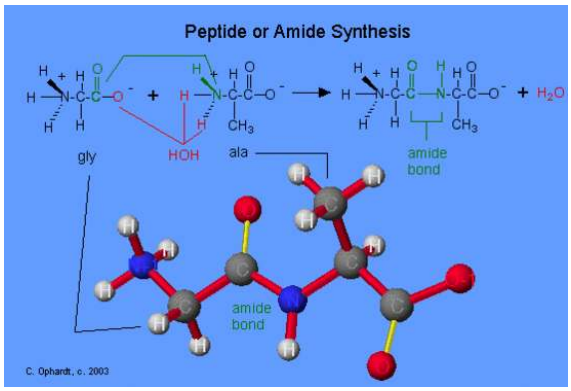
- An amino acid is a compound that contains both an amine group ($-NH_2$) and a carboxyl group ($-COOH$) in the same molecule.
- The nature of an amino acid's side chain accounts for the variability in chemical and physical properties of amino acids.
- There are 20 amino acids formed and used by living organisms.

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9.3.1: Peptide Bonds

The formation of peptides is nothing more than the application of the amide synthesis reaction. By convention, the amide bond in the peptides should be made in the order that the amino acids are written. The amine end (N terminal) of an amino acid is always on the left, while the acid end (C terminal) is on the right. The reaction of glycine with alanine to form the dipeptide glyclalanine is written as shown in the graphic on the left. Oxygen (red) from the acid and hydrogens (red) on the amine form a water molecule. The carboxyl oxygen (green) and the amine nitrogen (green) join to form the amide bond.



If the order of listing the amino acids is reversed, a different dipeptide is formed such as alaninylglycine.

? Exercise 9.3.1.1

Write the reactions for:

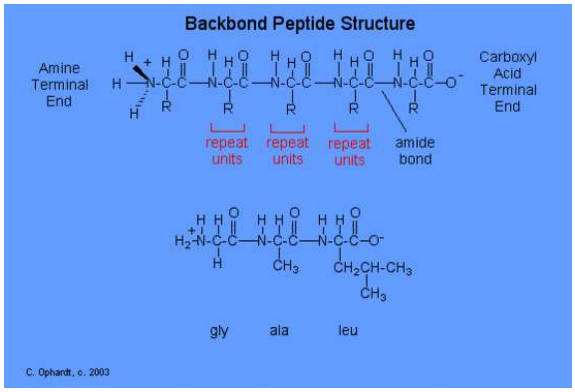
a. ala + gly ---> Answer graphic
b. phe + ser ----> Answer graphic

Salt Formation Contrast

The salt formation reaction is simply the transfer of the -H (positive ion) from the acid to the amine and the attraction of the positive and negative chagres. The acid group becomes negative, and the amine nitrogen becomes positive because of the positive hydrogen ion. No water is formed and there is only one product, the salt.

Backbone Peptide or Protein Structure

The structure of a peptide can be written fairly easily without showing the complete amide synthesis reaction by learning the structure of the "backbone" for peptides and proteins. The peptide backbone consists of repeating units of "N-H 2, CH, C double bond O; N-H 2, CH, C double bond O; etc. After the backbone is written, go back and write the specific structure for the side chains as represented by the "R" as gly-ala-leu for this example. The amine end (N terminal) of an amino acid is always on the left (gly), while the acid end (C terminal) is on the right (leu).



? Exercise 9.3.1.2

Write the tripeptide structure for val-ser-cys. First write the "backbone" and then add the specific side chains. Answer graphic

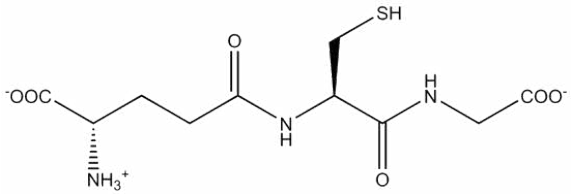
? Exercise 9.3.1.3

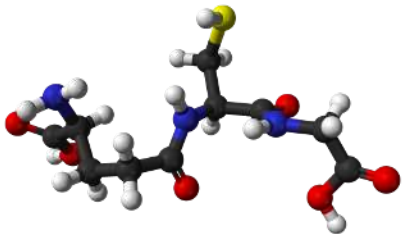
Write the structure for the tripeptide:

1. a) glu-cys-gly ---> Answer graphic
2. b) phe-tyr-asn ---> Answer graphic

Glutathione

Glutathione is an important tripeptide present in significant concentrations in all tissues. It contains glutamic acid, cysteine, and glycine. What is unusual about the structure of glutathione (bottom figure below? Compare it to a "normal" tri peptide of glu-cys-gly (top graphic). Instead of the usual backbone, the carboxyl acid "side chain" is part of the backbone peptide structure. The normal carboxyl group is the so called side chain in this case.





The function of glutathione is to protect cells from oxidizing agents which might otherwise damage them. The oxidizing agents react with the -SH group of cysteine of the glutathione instead of doing damage elsewhere. Many foreign chemicals get attached to glutathione, which is really acting as a detoxifying agent.

Contributors

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9.3.2: Proteins and Amino Acids

Proteins, from the Greek *proteios*, meaning first, are a class of organic compounds which are present in and vital to every living cell. In the form of skin, hair, callus, cartilage, muscles, tendons and ligaments, proteins hold together, protect, and provide structure to the body of a multi-celled organism. In the form of enzymes, hormones, antibodies, and globulins, they catalyze, regulate, and protect the body chemistry. In the form of hemoglobin, myoglobin and various lipoproteins, they effect the transport of oxygen and other substances within an organism.

Contributors and Attributions

William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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9.4: Nucleic Acids

Following the initial isolation of insulin in 1921, diabetic patients could be treated with insulin obtained from the pancreases of cattle and pigs. Unfortunately, some patients developed an allergic reaction to this insulin because its amino acid sequence was not identical to that of human insulin. In the 1970s, an intense research effort began that eventually led to the production of genetically engineered human insulin—the first genetically engineered product to be approved for medical use. To accomplish this feat, researchers first had to determine how insulin is made in the body and then find a way of causing the same process to occur in nonhuman organisms, such as bacteria or yeast cells. Many aspects of these discoveries are presented in this chapter on nucleic acids.



Figure **9.4.1**: A vial of insulin. It has been given a trade name, Actrapid, by the manufacturer. (Public Domain; Mr Hyde).

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9.4.1: Nucleotides

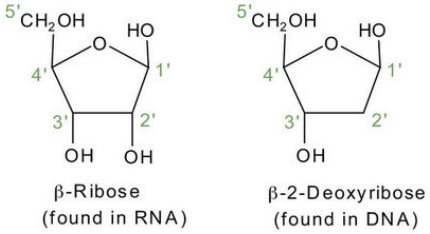
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

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 **9.4.1.1**).

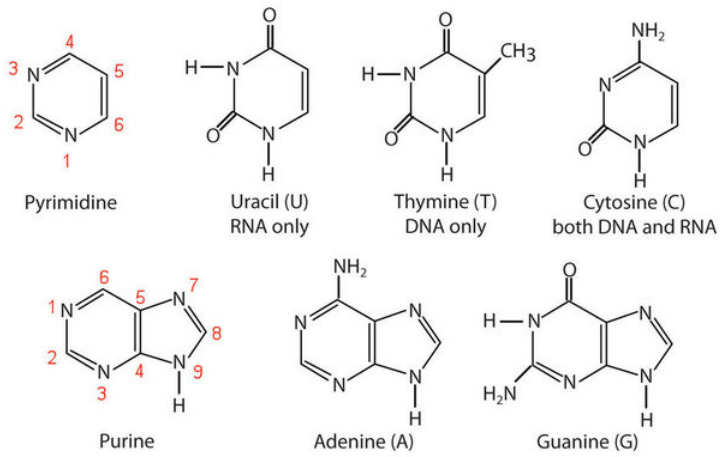


Figure **9.4.1.1**: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table **9.4.1.1** summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table **9.4.1.1**: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure **9.4.1.2**.

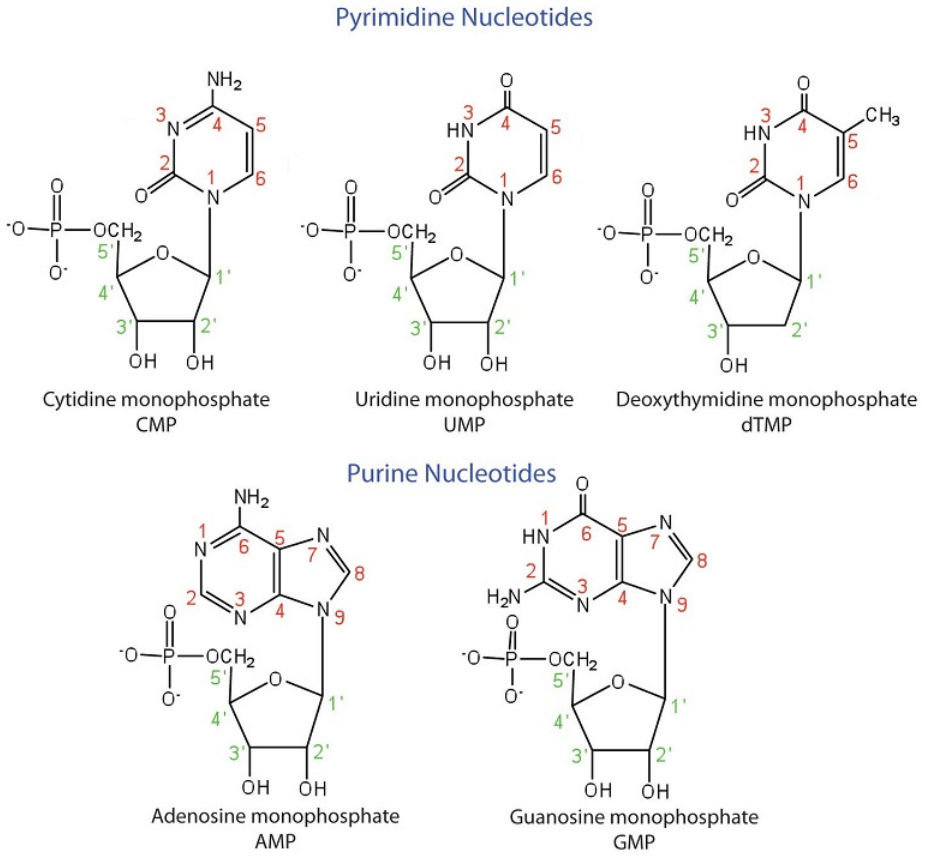


Figure **9.4.1.2**: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure **9.4.1.3**, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

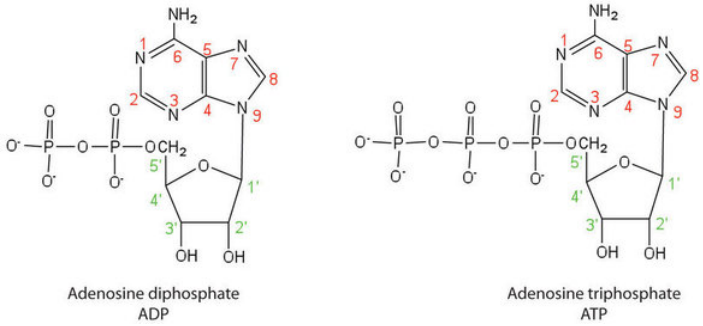


Figure **9.4.1.3**: Structures of Two Important Adenine-Containing Nucleotides

Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

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9.4.2: Nucleic Acid Structure

Skills to Develop

- Identify the two types of nucleic acids and the function of each type.
- Describe how nucleotides are linked together to form nucleic acids.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure **9.4.2.1**). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

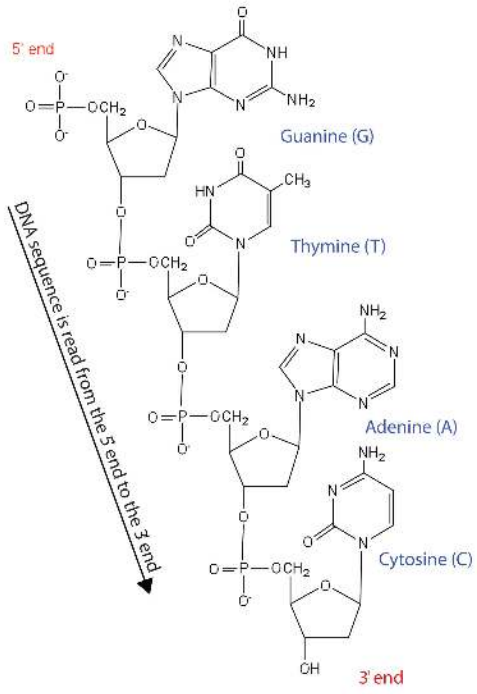


***Figure* 9.4.2.1** *Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2', and uracil would replace thymine.*

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure **9.4.2.1**) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are

deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure **9.4.2.1** would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure **9.4.2.2**).

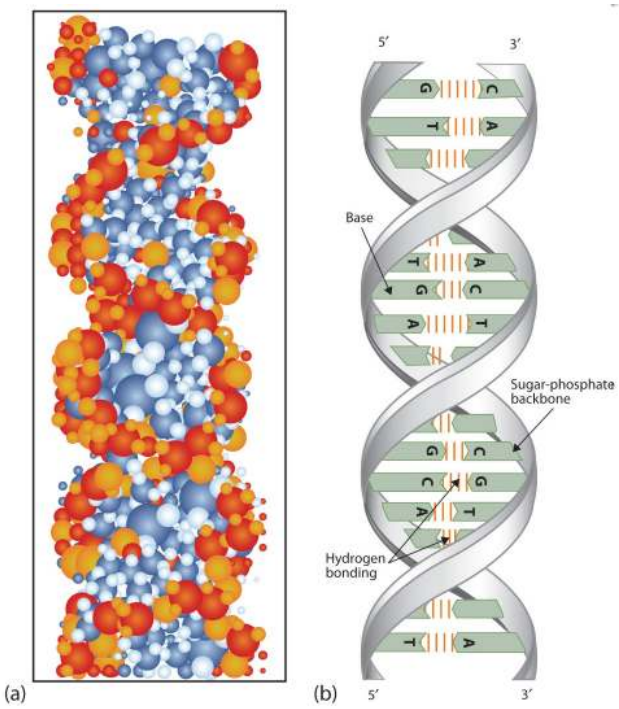


***Figure* 9.4.2.2** *DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.*

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure **9.4.2.3** shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

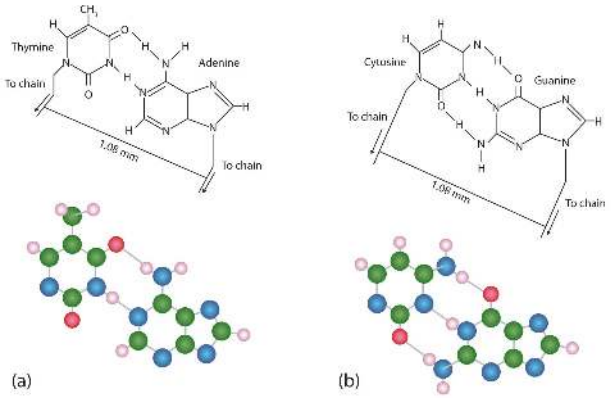


***Figure* 9.4.2.3** *Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.*

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure **9.4.2.4**. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure **9.4.2.3** is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

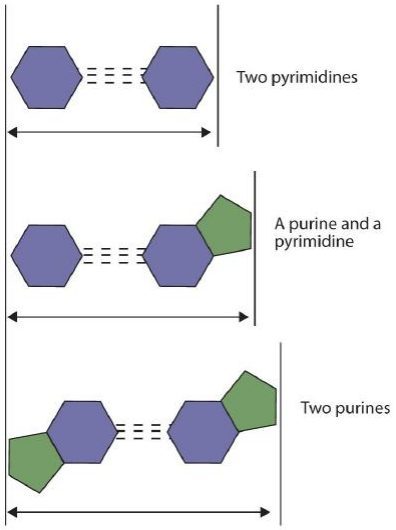


***Figure* 9.4.2.4** *Difference in Widths of Possible Base Pairs*

Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

Concept Review Exercises

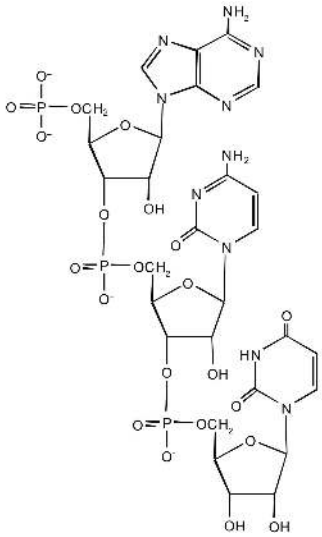
1.
   a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

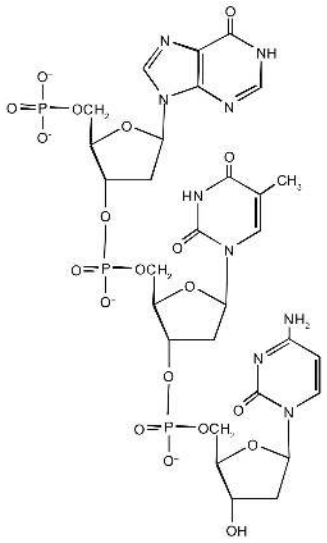
1.
   a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.



3. Which nitrogenous base in DNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine
   c. guanine
   d. thymine

4. Which nitrogenous base in RNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine
   c. guanine
   d. thymine

5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

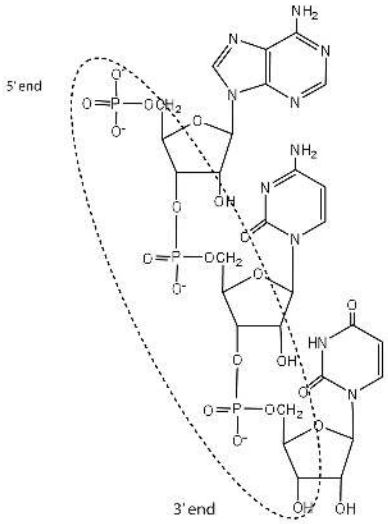
   5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′

6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers

1.



c. ACU

3.

a. guanine
b. thymine
c. cytosine
d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

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CHAPTER OVERVIEW

10: Solids, Liquids, and Gases, Solutions and energy

Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves.

We normally experience carbon dioxide (CO_2) as a gas, but if it were cooled down to about −78°C, it would become a solid. The everyday term for solid carbon dioxide is dry ice.

Why “dry” ice? Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves. The cold carbon dioxide gas is also heavier than air (because it is cold and more dense), so people in the presence of dry ice should be in a well-ventilated area.



Figure 10.1: Dry ice. (CC BY SA 3.0 unported; ProjectManhattan).

Dry ice has several common uses. Because it is so cold, it is used as a refrigerant to keep other things cold or frozen (e.g., meats or ice cream). In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It also has dermatological applications (e.g., freezing off warts). Organs for transplant are kept cool with dry ice until the recipient of the new organ is ready for surgery. In this respect, carbon dioxide is much like water—more than one phase of the same substance has significant uses in the real world.

10.1: Intermolecular Forces
10.2: Solubility and Pollution
10.3: Properties of Liquids
10.3.1: Water Cycle
10.3.2: Water Pollution
10.3.3: Biological Contamination of Water
10.3.4: Chemical Contamination of Water
10.3.5: Water Treatment
10.3.6: PBBs
10.4: Solids

10.4.1: Fats and Lipids in Bioamplification
10.5: Prelude to Gases
10.5.1: Kinetic Theory of Gases
10.6: Prelude to Solutions
10.6.1: Definitions
10.7: Introduction to energy
10.7.1: Energy and Chemical Bonds
10.7.2: Exothermic and Endothermic Reactions
10.7.3: Phase Changes
10.7.4: Phase Diagrams
10.S: Liquids and Intermolecular Forces (Summary)

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10.1: Intermolecular Forces

Learning Objective

- Relate phase to intermolecular forces.

Why does a substance have the phase that it does? The preferred phase of a substance at a given set of conditions is a balance between the energy of the particles and intermolecular forces (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

What forces define intermolecular interactions? There are several. A force present in all substances with electrons is the **dispersion force** (sometimes called the *London dispersion force*, after the physicist Fritz London, who first described this force in the early 1900s). This interaction is caused by the instantaneous position of an electron in a molecule, which temporarily makes that point of the molecule negatively charged and the rest of the molecule positively charged. In an instant, the electron is now somewhere else, but the fleeting imbalance of electric charge in the molecule allows molecules to interact with each other. As you might expect, the greater the number of electrons in a species, the stronger the dispersion force; this partially explains why smaller molecules are gases and larger molecules are liquids and solids at the same temperature. (Mass is a factor as well.)

Molecules with a permanent dipole moment experience **dipole-dipole interactions,** which are generally stronger than dispersion forces if all other things are equal. The oppositely charged ends of a polar molecule, which have partial charges on them, attract each other (Figure 10.1.1). Thus, a polar molecule such as CH_2Cl_2 has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like CF_4 (145 K, or −128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

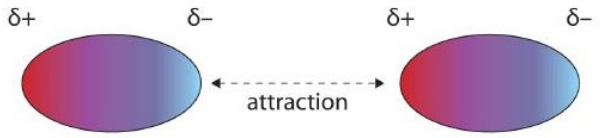


Figure 10.1.1: Dipole-Dipole Interactions. Oppositely charged ends of polar molecules attract each other.
2 ovals with partial positive left & right sides are attracted to each other. The right of oval 1 is attracted to the left of oval 2.

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H_2O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H_2S, is 233 K (−60°C). This is because H_2O molecules experience hydrogen bonding, while H_2S molecules do not. This strong attraction between H_2O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (Figure 10.1.2).

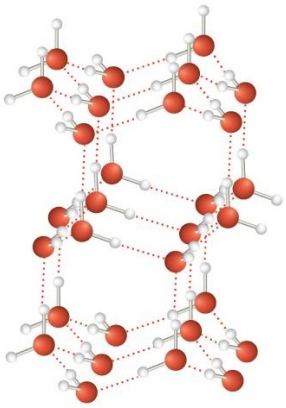


Figure **10.1.2**: Hydrogen Bonding. When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

Example 10.1.1

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

1. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
2. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
3. 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 10.1.1

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answers

a. hydrogen bonding
b. dipole-dipole interactions

The preferred phase a substance adopts can change with temperature. At low temperatures, most substances are solids (only helium is predicted to be a liquid at absolute zero). As the temperature increases, those substances with very weak intermolecular forces become gases directly (in a process called *sublimation*, which will be discussed in Section 10.3). Substances with weak interactions can become liquids as the temperature increases. As the temperature increases even more, the individual particles will have so much energy that the intermolecular forces are overcome, so the particles separate from each other, and the substance becomes a gas (assuming that their chemical bonds are not so weak that the compound decomposes from the high temperature). Although it is difficult to predict the temperature ranges for which solid, liquid, or gas is the preferred phase for any random substance, all substances progress from solid to liquid to gas (in that order) as temperature increases.

Summary

- All substances experience dispersion forces between their particles.
- Substances that are polar experience dipole-dipole interactions.

- Substances with covalent bonds between an H atom and N, O, or F atoms experience hydrogen bonding.
- The preferred phase of a substance depends on the strength of the intermolecular force and the energy of the particles.

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10.2: Solubility and Pollution

A solution may be gases, liquids, or solids and is composed of a solute and solvent. The solvent is usually the part of the solution that is present in the greatest amount. The solute is the substance that is dissolving in the solvent and is present in a smaller amount. Solubility is the amount of solute needed to form a saturated solution for a given quantity of solvent at a given temperature to produce a saturated solution.[1] Solubility versus temperature dependent graphs are often created and show that for most ionic substances their solubility increases with temperature. In addition, the solubility of ionic compounds at a particular temperature varies due to interactions between the solute and solvent. In addition, solubility is affected by the intermolecular bonding that occurs in the ionic compounds.

$$\text{Solubility} = \frac{\text{grams of solute}}{\text{100 grams of solvent}}$$

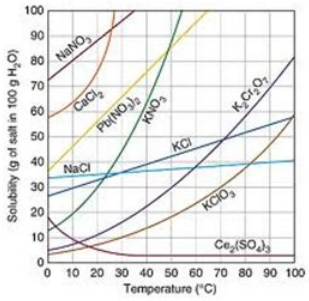


Figure **10.2.1**. *Solubility curve of ionic compounds.*[2]

A saturated solution contains the maximum amount of solute for a given amount of solvent at a constant temperature. A saturated solution is in a state of dynamic equilibrium; no additional solute will dissolve if added to the solvent. An unsaturated solution contains less solute than a saturated solution; therefore it has the capacity to dissolve more solute. A supersaturated solution contains more solute than it can theoretically hold at a given temperature. A supersaturated solution is made by adding additional solute and heating the solution and slowly cooling undisturbed. Sometimes in order for crystallization to occur, a seed crystal must be introduced and the crystallization process is quite fast and dramatic.



Figure **10.2.2**. *Crystallization of a supersaturated solution after the addition of a seed crystal.*[3]

The solubility of most solid and liquid solutions increases as the temperature increases. This is not true for gases; rather the solubility of gases decreases as the temperature increases. The reason for the decrease in solubility is related to the movement of the molecules. Temperature is a measure of the average kinetic energy of the molecules of a substance. An increase in temperature results in an increase in the kinetic energy of the molecules and an increase in thermal energy. The higher kinetic energy causes more motion in the molecules, which causes the intermolecular attraction to decrease and the gas molecules of solute can escape the solution.[1] This can easily be seen when an open can of soda in placed at room temperature or in a cool refrigerator. If an individual would taste the two cans, of soda the can at room temperature would taste very “flat” since more of the “fizz” which is carbon dioxide has escaped the can. Boiled water also tastes “flat” because more of the oxygen gas has been removed.

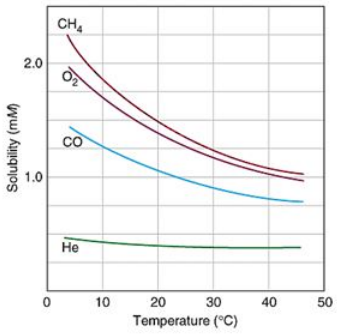


Figure **10.2.3**. *A graph of the solubility of gases versus temperature, showing that as the temperature of the solution increases the solubility of a gas decreases.*[4]

Thermal pollution occurs when the temperature of a natural body of water, such as, river, lake or ocean is altered. This alters the natural environment and impacts the organisms that live or rely on an aquatic ecosystem. Thermal pollution is associated with electrical power plants and industrial factories that that use fossil fuels or nuclear power; this results in the release of large amounts of excess thermal energy.[5] Water absorbs the energy and is converted to steam, which is used to turn turbines and generate electricity. As some point, the water will need to be dumped back into nearby river, lake, or ocean and if not properly cooled, it can increase the temperature of the natural body of water. Thermal pollution can also involve putting colder the normal water into a nearby body of water.

Elevated water temperatures can also arise from deforestation and urbanization which causes changes in the landscape surrounding a body of water. When trees surrounding a body of water are removed, the now unshaded water can increase its temperature by as much as 10 ^{o}C. Thermal pollution can even result when the landscape away from the body of water is altered. These changes in landscape may cause erosion, changes in water volume, and pollutants that may change the composition of the water. For example, muddy water absorbs more energy from the sun than clear water.

Every response of an aquatic organism from incubation of the egg, to feeding activity, digestive and metabolic processes, reproduction, geographic distribution, and even survival occurs due to the thermal range by their immediate environment. The solubility of gases in water plays a major role in the survival of ectotherms, such as fish. Since an increase in temperature contributes to a decline in the solubility of gases in water; water that is of a higher temperature lacks oxygen. Therefore, many fish are only capable of existing in waters of a lower temperature where ample oxygen exists. Another problem that may occur due to thermal pollution is a limited metabolic range of many aquatic organisms. Many living organisms have metabolic enzymes that control the oxidation of organic food matter. Metabolic enzymes can only function in a narrow range of temperatures, and most enzymes show an optimum temperature in which they reach maximum rate of catalytic activity.[5] Small changes in temperature can prove to be deadly for fish. Thermal pollution can also decrease the biodiversity of an ecosystem and allow for the creation of environment that can be invaded by alien aquatic species that may disrupt or destroy an entire ecosystem.[5]

Sea turtles in the San Diego Bay are example of how temperature may have affected the metabolic rate of an organism. In 1956, an electric power plant was built near the San Diego Bay, and is thought to be the reason for a colony of East Pacific green turtles living in the Bay. These turtles chose this location as their habitat; in spite of the fact, that it is one of the busiest harbors in the world. The power plant discharges the water that is 15 degrees above the normal temperature of the water in the Bay.[6] Researchers think that the warm water is the attraction for the turtles but due a decrease in oxygen in the water, the metabolic rate of the turtles is increased. The Eastern Pacific green turtles in this region are supersized, with some weighing as much as 550 pounds.[6] The sizes of these turtles are unprecedented in their enormity and are almost the double the normal size records of the same species in other habitats.[6] Carl Mayhugli, a Prescott College graduate, is working on his Masters on the movements and habitats of these turtles. He theorizes that the turtles are able to reach such massive size because the warmer water allows them to continue to forage for food when most sea turtles due to cooler water enter a state of hibernation called torpor.[6] The warm water allows eelgrass and algae to grow which provides a supplement to the turtle's normal diet of tube worms, sea hares, jellyfish and other slow-moving soft-bodied sea creatures.[6] The massive turtles are able to increase their food intake by increasing their herbivory diet. The power plant is set to be decommissioned in the next several years but the hope is they will continue to keep the bay as their nesting location.

From ChemPRIME: 10.15: Saturated and Supersaturated Solutions

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10.3: Properties of Liquids

Learning Objective

- Define the vapor pressure of liquids.
- Explain the origin of both surface tension and capillary action.

There are some properties that all liquids, including water, have. All liquids have a certain portion of particles with enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (Figure **10.3.1**). The formation of a gas from a liquid at temperatures below the boiling point is called **evaporation**. At these temperatures, the material in the gas phase is called **vapor**, rather than gas; the term *gas* is reserved for when the gas phase is the stable phase.

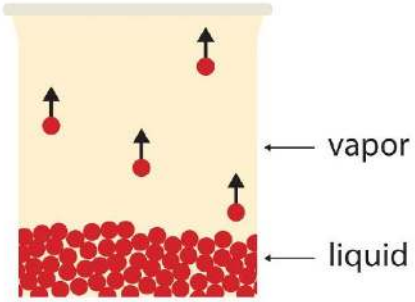


Figure **10.3.1**: Evaporation. Some particles of a liquid have enough energy to escape the liquid phase to become a vapor.

If the available volume is large enough, eventually all the liquid will become vapor. But if the available volume is not enough, eventually some of the vapor particles will reenter the liquid phase (Figure **10.3.2** Equilibrium). At some point, the number of particles entering the vapor phase will equal the number of particles leaving the vapor phase, so there is no net change in the amount of vapor in the system. We say that the system is *at equilibrium*. The partial pressure of the vapor at equilibrium is called the *vapor pressure of the liquid*.

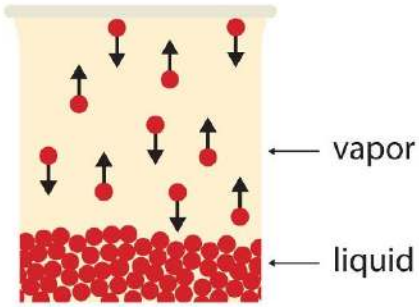


Figure **10.3.2**: Equilibrium. At some point, the number of particles entering the vapor phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.

Understand that the liquid has not stopped evaporating. The reverse process—condensation—is occurring as fast as evaporation, so there is no net change in the amount of vapor in the system. The term **dynamic equilibrium** represents a situation in which a process still occurs, but the opposite process also occurs at the same rate, so that there is no net change in the system.

The vapor pressure for a substance is dependent on the temperature of the substance; as the temperature increases, so does the vapor pressure. Figure **10.3.3** - Plots of Vapor Pressure versus Temperature for Several Liquids, is a plot of vapor pressure versus temperature for several liquids. Having defined vapor pressure, we can also redefine the *boiling point* of a liquid: the temperature at which the vapor pressure of a liquid equals the surrounding environmental pressure. The normal vapor pressure, then, is the temperature at which the vapor pressure is 760 torr, or exactly 1 atm. Thus boiling points vary with surrounding pressure, a fact that can have large implications on cooking foods at lower- or higher-than-normal elevations. Atmospheric pressure varies significantly with altitude.

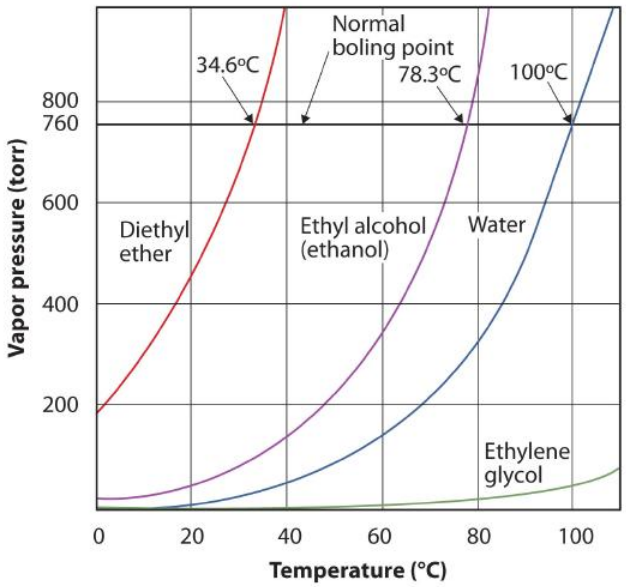


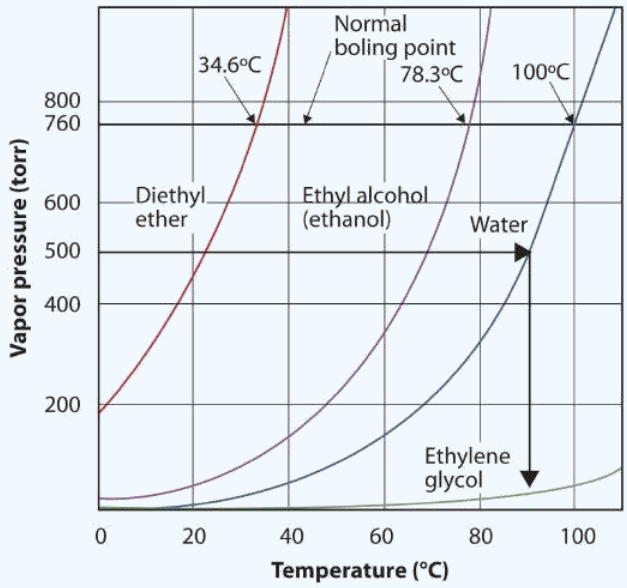
Figure **10.3.3**: Plots of Vapor Pressure versus Temperature for Several Liquids. The vapor pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.

Example 10.3.1

Use Figure **10.3.3** to estimate the boiling point of water at 500 torr, which is the approximate atmospheric pressure at the top of Mount Everest.

Solution

See the accompanying figure. Five hundred torr is between 400 and 600, so we extend a line from that point on the *y*-axis across to the curve for water and then drop it down to the *x*-axis to read the associated temperature. It looks like the point on the water vapor pressure curve corresponds to a temperature of about 90°C, so we conclude that the boiling point of water at 500 torr is 90°C.



By reading the graph properly, you can estimate the boiling point of a liquid at different temperatures.

https://chem.libretexts.org/@go/page/209046

? Exercise 10.3.1

Use Figure **10.3.3** to estimate the boiling point of ethanol at 400 torr.

Answer

about 65°C

The vapor pressure curve for water is not exactly zero at the melting point 0°C. Even ice has a vapor pressure—that is why it sublimes over time. However, the vapor pressures of solids are typically much lower than that of liquids. At −1°C, the vapor pressure of ice is 4.2 torr. At a freezer temperature of 0°F (−17°C), the vapor pressure of ice is only 1.0 torr; so-called deep freezers can get down to −23°C, where the vapor pressure of ice is only 0.6 torr.

All liquids share some other properties as well. **Surface tension** is an effect caused by an imbalance of forces on the atoms at the surface of a liquid, as shown in Figure **10.3.4**. The blue particle in the bulk of the liquid experiences intermolecular forces from all around, as illustrated by the arrows. However, the yellow particle on the surface does not experience any forces above it because there are no particles above it. This leads to an imbalance of forces, called surface tension.

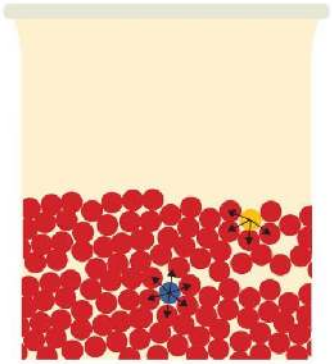


Figure **10.3.4** Surface Tension. Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.

Surface tension is responsible for several well-known behaviors of liquids, including water. Liquids with high surface tension tend to bead up when present in small amounts (Figure **10.3.5**).



Figure **10.3.5** Effects of Surface Tension © Thinkstock. Water on the surface of this apple beads up due to the effect of surface tension.

Surface tension causes liquids to form spheres in free fall or zero gravity. Surface tension is also responsible for the fact that small insects can "walk" on water. Because of surface tension, it takes energy to break the surface of a liquid, and if an object (such as an insect) is light enough, there is not enough force due to gravity for the object to break through the surface, so the object stays on top of the water (Figure **10.3.6**). Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.



Figure **10.3.6** Walking on Water. Small insects can actually walk on top of water because of surface tension effects. (Unsplash License; Miguel Alcântara via unsplash)

The fact that small droplets of water bead up on surfaces does not mean that water—or any other liquid—does not interact with other substances. Sometimes the attraction can be very strong. **Adhesion** is the tendency of a substance to interact with other substances because of intermolecular forces, while **cohesion** is the tendency of a substance to interact with itself. If cohesive forces within a liquid are stronger than adhesive forces between a liquid and another substance, then the liquid tends to keep to itself; it will bead up. However, if adhesive forces between a liquid and another substance are stronger than cohesive forces, then the liquid will spread out over the other substance, trying to maximize the interface between the other substance and the liquid. It is said that the liquid *wets* the other substance.

Adhesion and cohesion are important for other phenomena as well. In particular, if adhesive forces are strong, then when a liquid is introduced to a small-diameter tube of another substance, the liquid will move up or down in the tube, as if ignoring gravity. Because tiny tubes are called capillaries, this phenomenon is called **capillary action.** For example, one type of capillary action, *capillary rise*, is seen when water or water-based liquids rise up in thin glass tubes (like the capillaries sometimes used in blood tests), forming an upwardly curved surface called a **meniscus**. Capillary action is also responsible for the "wicking" effect that towels and sponges use to dry wet objects; the matting of fibers forms tiny capillaries that have good adhesion with water. Cotton is a good material for this; polyester and other synthetic fabrics do not display similar capillary action, which is why you seldom find rayon bath towels. A similar effect is observed with liquid fuels or melted wax and their wicks. Capillary action is thought to be at least partially responsible for transporting water from the roots to the tops of trees, even tall ones.

On the other hand, some liquids have stronger cohesive forces than adhesive forces. In this case, in the presence of a capillary, the liquid is forced down from its surface; this is an example of a type of capillary action called *capillary depression*. In this case, the meniscus curves downward. Mercury has very strong cohesive forces; when a capillary is placed in a pool of mercury, the surface of the mercury liquid is depressed (Figure **10.3.7**).

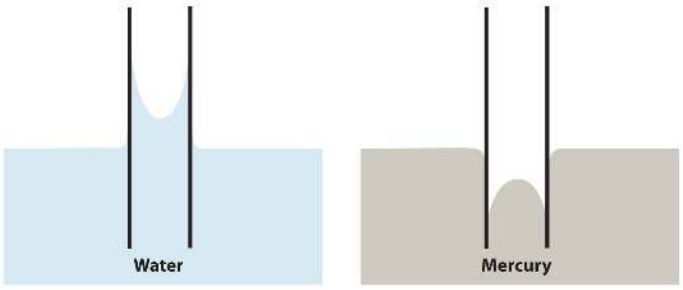


Figure **10.3.7**: Capillary Action. (a) Capillary rise is seen when adhesion is strong, such as with water in a thin glass tube. (b) Capillary depression is seen when cohesive forces are stronger than adhesive forces, such as with mercury and thin glass tubes.

Chemistry is Everywhere: Waxing a Car

Responsible car owners are encouraged to wax their cars regularly. In addition to making the car look nicer, it also helps protect the surface, especially if the surface is metal. Why?

The answer has to do with cohesion and adhesion (and, to a lesser extent, rust). Water is an important factor in the rusting of iron, sometimes used extensively in outer car bodies. Keeping water away from the metal is one way to minimize rusting. A coat of paint helps with this. However, dirty or scratched paint can attract water, and adhesive forces will allow the water to wet the surface, maximizing its contact with the metal and promoting rust.



Figure **10.3.8**: Waxing a car. Droplets of water on a freshly waxed car do not wet the car well because of low adhesion between water and the waxed surface. This helps protect the car from rust. (Unsplash License; Yuvraj Singh via Unspash)

Wax is composed of long hydrocarbon molecules that do not interact well with water. (Hydrocarbons are compounds with C and H atoms; for more information on hydrocarbons, see Chapter 16). That is, a thin layer of wax will not be wetted by water. A freshly waxed car has low adhesive forces with water, so water beads up on the surface, as a consequence of its cohesion and surface tension. This minimizes the contact between water and metal, thus minimizing rust.

Summary

- All liquids evaporate.
- If volume is limited, evaporation eventually reaches a dynamic equilibrium, and a constant vapor pressure is maintained.
- All liquids experience surface tension, an imbalance of forces at the surface of the liquid.
- All liquids experience capillary action, demonstrating either capillary rise or capillary depression in the presence of other substances.

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10.3.1: Water Cycle

Learning Objectives

- Recall the percentages of fresh and salt water sources on Earth.
- Know the processes and phases of the water (hydrologic) cycle.
- Understand hydrologic terms: stream, pond, river, reservoir, wetland, aquifer, and ocean.
- Recall the large consumers of water in the United States and in the world.

Water is composed of one oxygen atom bonded with two hydrogen atoms (H_2O). Despite its simplicity, water has remarkable properties. It expands when it freezes, has high surface tension (because of the polar nature of the molecules that stick together), and has a high boiling point for a liquid. Without water, life might not be able to exist on Earth, and this planet would not have the tremendous complexity and diversity that we see.



Figure **10.3.1.1**: This Florentine Bell Tower is one of Furman University most beloved landmarks. The original Furman Bell Tower was built in 1854 on what used to be the men's campus in Downtown Greenville. During that time,the bells rang to signal the start of classes and to celebrate victories for the athletic teams. Image courtesy of Elizabeth R. Gordon.

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 **10.3.1.2**). 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 atmosphere is known as a **reservoir**. A water molecule may pass through a reservoir very quickly or may remain for much longer. The amount of time a molecule stays in a reservoir is known as its **residence time**.

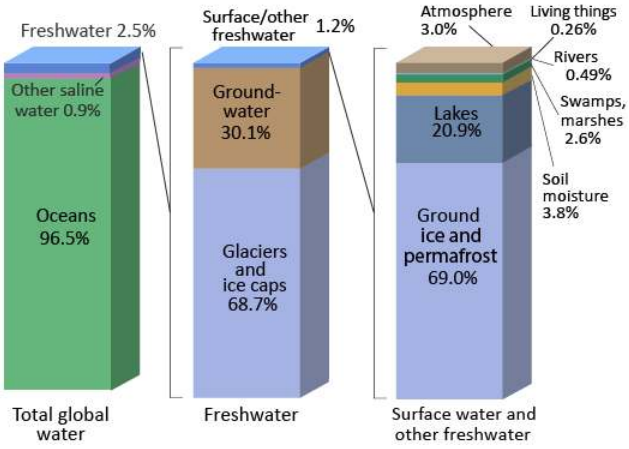


Figure* 10.3.1.2*: *The distribution of Earth's water. In the first bar, notice how only 2.5% of Earth's water is freshwater - the amount needed for life to survive. The middle bar shows the breakdown of freshwater. Almost all of it is locked up in ice and in the ground. Only a little more than 1.2% 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 Hydrologic Cycle

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 **hydrologic (water) cycle** (Figure **10.3.1.3**).

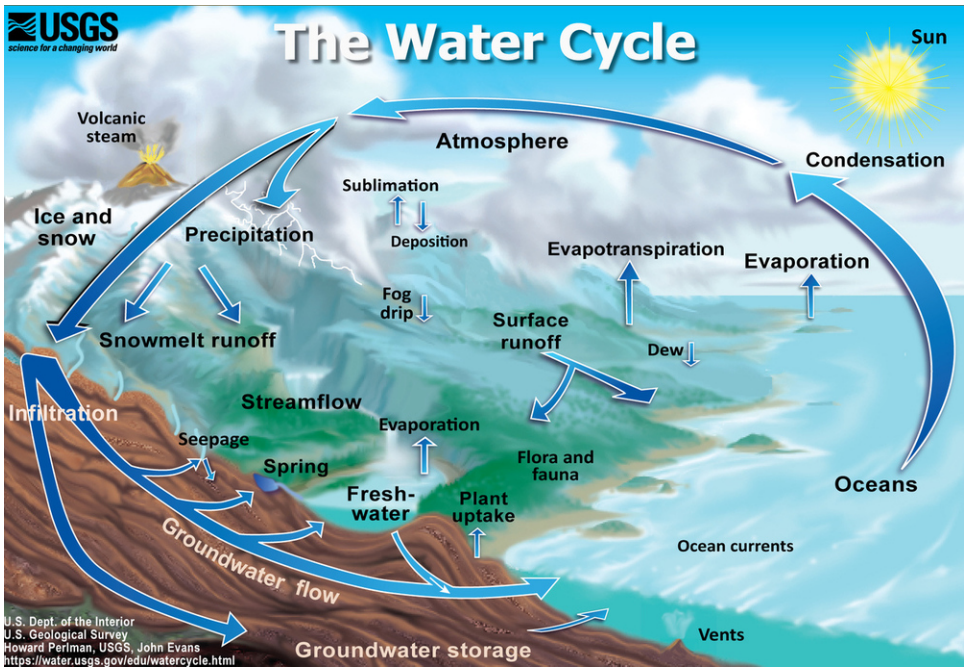


Figure **10.3.1.3**: *Because it is a cycle, the water cycle has no beginning and no end. Earth's water is always in movement, and the natural water cycle, also known as the hydrologic cycle, describes the continuous movement of water on, above, and below the surface of the Earth. Water is always changing states between liquid, vapor, and ice, with these processes happening in the blink of an eye and over millions of years.*

The Sun, while many millions of kilometers away, provides the energy that drives the water cycle. It impacts the water cycle by supplying the energy needed for evaporation. Most of Earth's water is stored in the oceans where it can remain for hundreds or thousands 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** to become tiny droplets of liquid. The droplets gather in clouds, which are blown around the globe by the wind. As the water droplets in the clouds collide and grow, they fall from the sky as **precipitation**(rain, sleet, hail, or snow). Precipitation can fall back into the ocean and/or land surface.



Figure **10.3.1.4**: Snow is one form of precipitation and a key transport mechanism in the water cycle. Image courtesy of Elizabeth R. Gordon

When water falls from the sky as rain it may enter streams and rivers that flow downward to oceans and lakes. Water that falls as snow may sit on a mountain for several months. Snow may become part of the ice in a glacier, where it may remain for hundreds or thousands of years. Snow and ice may go directly back into the air by **sublimation**, the process in which solid changes directly into a gas without first becoming a liquid. Although you probably have not seen water vapor sublime from a glacier, you may have seen dry ice sublime in the air.

Snow and ice slowly melt over time to become liquid water, which provides a steady flow of fresh water to streams, rivers, and lakes below. A water droplet falling as rain could also become part of a stream or a lake. At the surface, the water may eventually evaporate and reenter the atmosphere. A significant amount of water infiltrates into the ground. Soil moisture is an important reservoir for water (Figure **10.3.1.5**). Water may seep through dirt and rock below the soil through pores infiltrating the ground to go into Earth's groundwater system. Groundwater enters **aquifers** that may store fresh water for centuries. Alternatively, the water may come to the surface through springs or find its way back to the oceans.

Water trapped in soil is important for plants to grow. Plants and animals depend on water to live and they also play a role in the water cycle. Plants take up water from the soil and release large amounts of water vapor into the air through their leaves, a process is known as *transpiration*.

It is important to note that water molecules cycle around. If climate cools and glaciers and ice caps grow, there is less water for the oceans and sea level will fall. The reverse can also happen.

Components of the Hydrologic Cycle

Most precipitation falls in the form of rain, but there are other forms such as snow, hail, and sleet. Once it runs sufficiently, surface water runoff is generated when the ground is saturated or impervious. **Surface water** is a major component of the hydrological cycle and one that we interact with very regularly. It includes lakes, wetlands, storm water **runoff** (overland flow), ponds, potholes, rivers and streams.

Streams and Rivers

A river forms from water moving from a higher altitude to lower altitude, under the force of gravity. When rain falls on land, it can seep into the ground or become runoff (water running on the surface). If the water runs on the land surface, it can converge as it moves towards lower elevation. The converging runoff can concentrate into single channels of conveyance called creeks, stream, or rivers. Streams and rivers that join up to form a larger river are called **tributaries**, Figure **10.3.1.5**. The land area drained by a river and all its tributaries is called a **watershed** or river basin.

The area adjacent to a river that floods frequently is a called a **flood plain**. These regions temporarily store excess water during storm events and frequently contain fertile soils. Properly functioning flood plains reduce the negative impacts of floods (by reducing severity of flood) and they assist in filtering storm water which results in protecting the water quality of rivers. Also, flood plains act as areas of recharge for groundwater.



In South Carolina, the Santee River system flows throughout the state (Figure **10.3.1.6**). From North Carolina, the Saluda River runs through the South Carolina upstate region. The Saluda River converges with the Broad River south of Columbia, South Carolina. The combination of these two waterways form the Congaree River. Just north of Rock Hill, South Carolina, the Catawba River enters into the Wateree Reservoir. Once this water flows to Columbia, the Catawba River becomes the Wateree River. All of these rivers and water systems provide water for the upstate of South Carolina.

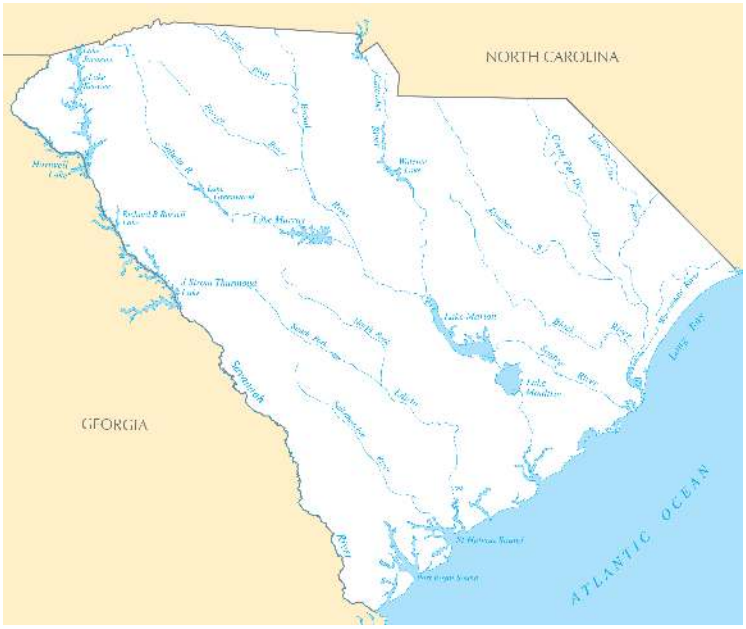


Figure **10.3.1.6**: Large rivers of South Carolina (CC BY-SA 1.0; http://mapsof.net)

Rivers are important for supplying water to the cities and populations of any state. In addition, rivers contain important biological communities and provide recreational opportunities like swimming, fishing, and white water rafting. Large cities, communities, factories, industries, and power stations are located along many rivers. It is, therefore, very important to protect the quality and integrity of rivers all over the world.

Lakes,reservoirs, and ponds

If water flows to a place that is surrounded by higher land on all sides, a lake will form. A smaller version of this type of aquatic system is called a pond. When dams are constructed to stop rivers from flowing, lakes are transformed into reservoirs. Once

constructed, reservoirs can provide water for consumption, cooling capacity for power plants, irrigation for agriculture, and recreation activities.

In the South Carolina upstate, Hartwell Reservoir provides cooling water for Oconee Nuclear Reactor Station. In addition, many South Carolina residents enjoy fishing, boating, and residing on the reservoir.

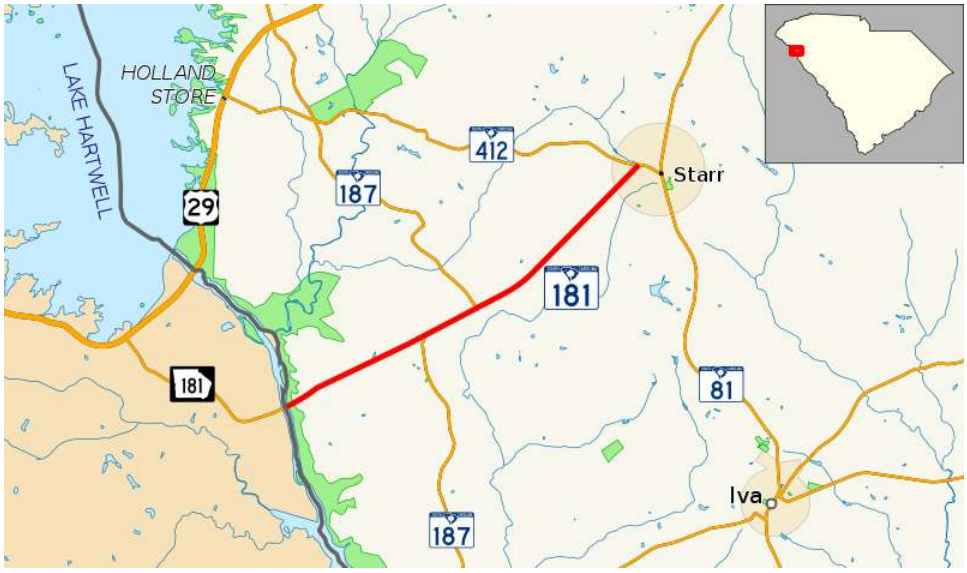


Figure **10.3.1.1**: Map of South Carolina Highway 101 (CC BY-SA 1.0 https://www.census.gov/cgi-bin/geo/s...iles/index.php;)

Wetland

A **wetland** is an area which is home to standing water for notable parts of the year, has saturated soils for a large part of the year and has plants that require large amounts of water to survive. Wetlands include swamps, marshes, and bogs. Wetlands are identified using three characteristics: soils (water-saturated soils are present), hydrology (shallow water table) and vegetation (wetland plants that are adapted to areas that are saturated with water for long periods of time). Wetlands are important areas of biological diversity and productivity. These are also important areas where geochemical and biological cycles/ processes are consistently taking place. For instance, wetlands are considered as areas of significant carbon sequestration (storage), which impacts global climate change. They also act as filters for storm-water runoff before it enters rivers and lakes.

Oceans

As you have probably already guessed, oceans are an important component of the hydrologic cycle because they store majority of all water on Earth (about 95%). Most of the major rivers drain into them. The five oceans covering the surface of the Earth are the Atlantic, Indian, Pacific, Arctic and the Southern Ocean (Figure **10.3.1.8**).

alt

Figure **10.3.1.8**: *The five oceans found on planet Earth. The Pacific Ocean is the largest. Source: upload.wikimedia.org/wikiped...n_drainage.png*

Approximately 90 % of the water that is evaporated into the hydrologic cycle comes from the ocean. The ocean contains many forms of life uniquely adapted to survive in this habitat. Unfortunately, humans have degraded the oceans and their life through pollution, excess fishing, carbon dioxide acidification, and resource exploitation.

Storage and Flow

Almost 99% of the available fresh water is found below the surface as groundwater. This resource results from recycling of water in the hydrologic cycle. When precipitation falls, water travels on the surface and some can infiltrate into the ground. Groundwater is replenished when water moves from the surface, through unsaturated rocks or sediment (**unsaturated**), all the way down the **saturated parts** (saturated zone) in a process called infiltration and becomes groundwater (Figure **10.3.1.10**). The top of the saturated portion is called the **water table**, which is the boundary between saturated and unsaturated zone.

Groundwater is found in **aquifers**, which are bodies of rock or sediment that store (and yield) large amounts of usable water in their pores. Aquifer productivity is controlled by **porosity** and **permeability**. Porosity is the percentage of open space in a rock or sediment body. Permeability is the ability of subsurface material to transmit fluids. Groundwater is found in the saturated zone of a rock body where all pores are filled with water. An important concept is that surface water always moves from higher elevation to lower elevation while groundwater always moves from higher energy (hydraulic head) to lower energy.



Figure **10.3.1.10**: Model of groundwater system showing the different components of an unconfined groundwater system: http://water.usgs.gov/edu/earthgwaquifer.html

Groundwater will continue to flow until it emerges as a spring, or discharges into surface water bodies on the land or in the ocean. To utilize groundwater, we drill holes (wells) into the ground and pump the water out.

Water Consumption

One of the most important natural resources is water. In some areas of the world, water sources are extremely limited or contaminated. If a geographical area lacks this resource, then agriculture and industry will have difficulty producing goods and foods. If water is contaminated, individuals who reside in these areas will be more likely to develop waterborne illnesses. Lack of water limits a consumer's ability to drink, eat, and bathe.

The table below illustrates who uses the majority of water sources. Be sure to note the differences between the United States and Global percentage applications.

***Table* 10.3.1.2**: *Water Use in the United States and Globally*

Use	United States	Global
Agriculture	34%	70%
Domestic (drinking, bathing)	12%	10%
Industry	5%	20%
Power plant cooling	49%	small

Contributors and Attributions

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10.3.2: Water Pollution

Learning Objectives

After reading this module, students should be able to

- understand the major kinds of water pollutants and how they degrade water quality
- understand how and why the lack of safe drinking water in some parts of the world is a major problem
- know what sewage treatment does and why it is important
- know why it is more difficult to remediate groundwater pollution than surface water pollution
- understand how we can work toward solving the crisis involving water pollution

The Water Pollution Crisis

The Module 7.3 described one aspect of the global water crisis, the water shortages that afflict many arid and densely populated areas. The global water crisis also involves water pollution, because to be useful for drinking and irrigation, water 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 improved (safe) drinking water (World Health Statistics, 2010) (See Figure **10.3.2.1**). At the same time, about 2.6 billion people (or 40% of world population) lived without improved sanitation (see Figure **10.3.2.2**), 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, e.g., hand washing with soap. Almost all of these deaths are in developing countries, and around 90% of them occur among children under the age of 5 (see Figure **10.3.2.3**). 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, 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. Some chemical pollutants have serious and well-known health effects; however, many others have poorly known long-term health effects. In the U.S. currently more than 40,000 water bodies fit the definition of “impaired” set by EPA (See Figure **10.3.2.4**), which means they could neither support a healthy ecosystem nor meet water quality standards. 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.

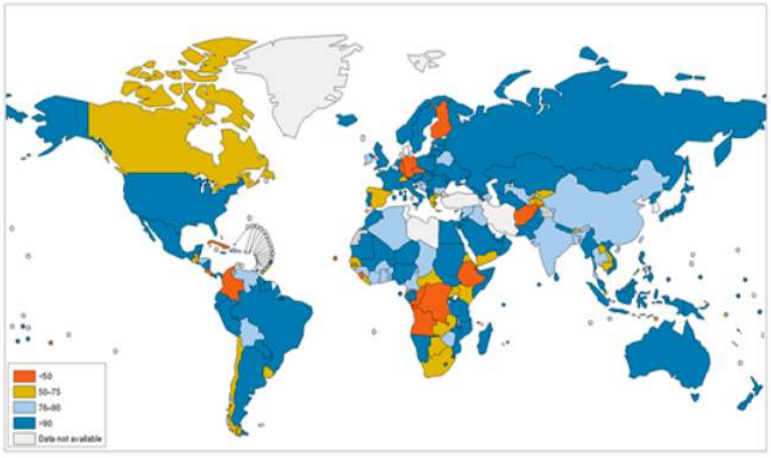


Figure **10.3.2.1** Proportion of Population by Country Using Improved Drinking Water Sources in 2008. Improved drinking water sources, e.g., household connections, public standpipes, boreholes, protected dug wells and springs, and rainwater collections, are defined as those more likely to provide safe water than unimproved water sources, e.g., unprotected wells and springs, vendor-provided water, bottled water (unless water for other uses is available from an improved source), and tanker truck-provided water. *Source:* *World Health Organization*

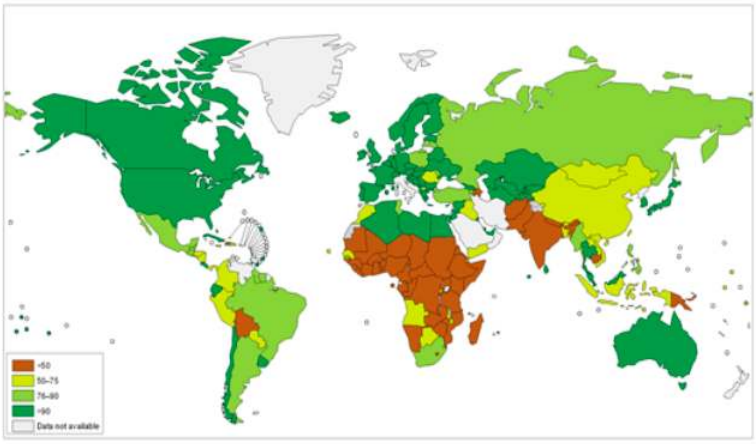


Figure **10.3.2.2** Proportion of Population by Country Using Improved Sanitation Facilities in 2008. Improved sanitation facilities, e.g., connection to public sewers or septic systems, pour-flush latrines, pit latrines, and ventilated improved pit latrines, are defined as those more likely to be sanitary than unimproved facilities, e.g., bucket latrines, public latrines, and open pit latrines. *Source:* World Health Organization

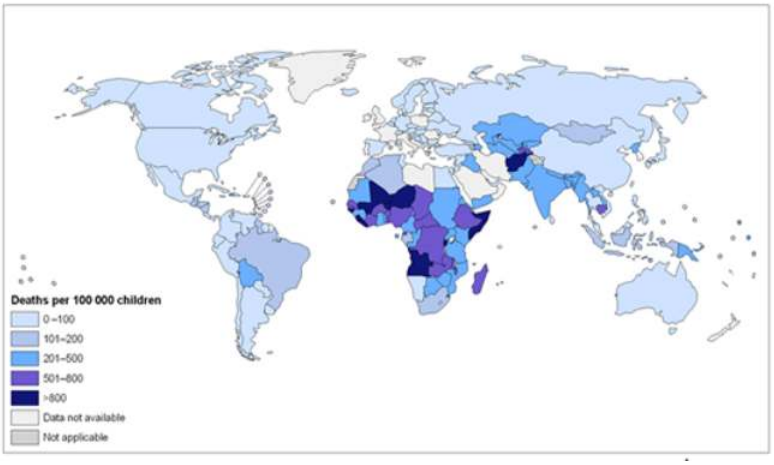


Figure **10.3.2.3** Deaths by Country from Diarrhea Caused by Unsafe Water, Unimproved Sanitation, and Poor Hygiene in Children Less than 5 Years Old, 2004. *Source:* World Health Organization

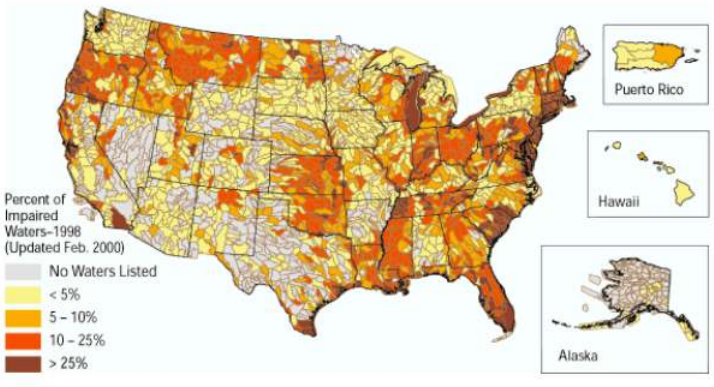


Figure **10.3.2.4** Percentage of Impaired Water Bodies in a Watershed by State in USA Based on US EPA Data in 2000. Map of watersheds containing impaired water bodies from the U.S. Environmental Protection Agency's 1998 list of impaired waters *Source:* U.S. Geological Survey

Water Chemistry Overview

Compared to other molecules of similar molecular weight, water (H_2O) has unique physical properties including high values for melting and boiling point, surface tension (water's cohesion, or "stickiness"), and capacity to dissolve soluble minerals, i.e., act as a solvent. These properties are related to its asymmetrical structure and *polar nature*, which means it is electrically neutral overall but it has a net positive charge on the side with the two hydrogen atoms and a net negative charge on the oxygen side (see Figure

10.3.2.5). This separation of the electrical charge within a water molecule results in *hydrogen bonds*with other water molecules, mineral surfaces (hydrogen bonding produces the water films on minerals in the unsaturated zone of the subsurface), and *dissolved ions* (atoms with a negative or positive charge). Many minerals and pollutants dissolve readily in water because water forms *hydration shells* (spheres of loosely coordinated, oriented water molecules) around ions.

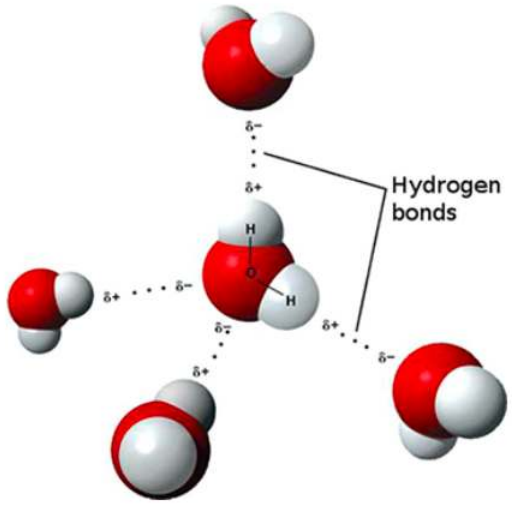


Figure 10.3.2.5 Structure of Water, Polar Charge of Water, and Hydrogen Bonds between Water Molecules. *Source: Michal Maňas at Wikimedia Commons*

Any natural water contains dissolved chemicals; some of these are important human nutrients, while others can be harmful to human health. The abundance of a water pollutant is commonly given in very small concentration units such as parts per million (ppm) or even parts per billion (ppb). An arsenic concentration of 1 ppm means 1 part of arsenic per million parts of water. This is equivalent to one drop of arsenic in 50 liters of water. To give you a different perspective on appreciating small concentration units, converting 1 ppm to length units is 1 cm (0.4 in) in 10 km (6 miles) and converting 1 ppm to time units is 30 seconds in a year. Total dissolved solids (TDS) represent the total amount of dissolved material in water. Average TDS (salinity) values for rainwater, river water, and seawater are about 4 ppm, 120 ppm, and 35,000 ppm. As discussed in Module 5.2, the most important processes that affect the salinity of natural waters are evaporation, which distills nearly pure water and leaves the dissolved ions in the original water, and chemical weathering, which involves mineral dissolution that adds dissolved ions to water. Fresh water is commonly defined as containing less than either 1,000 or 500 ppm TDS, but the US Environmental Protection Agency (EPA) recommends that drinking water not exceed 500 ppm TDS or else it will have an unpleasant salty taste.

Water Pollution Overview

Water pollution is the contamination of water by an excess amount of a substance that can cause harm to human beings and 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 (see Figure 10.3.2.6). Water pollutants can move through different water reservoirs, as the water carrying them progresses through stages of the water cycle (see Figure 10.3.2.7). Water residence time (the average time that a water molecule spends in a water reservoir) is very important to pollution problems because it affects pollution potential. Water in rivers has a relatively short residence time, so pollution usually is there only briefly. Of course, pollution in rivers may simply move to another reservoir, such as the ocean, where it can cause further problems. Groundwater is typically characterized by slow flow and longer residence time, which can make groundwater pollution particularly problematic. Finally, pollution residence time can be much greater than the water residence time because a pollutant may be taken up for a long time within the ecosystem or absorbed onto sediment.



Figure 10.3.2.6 Water Pollution. Obvious water pollution in the form of floating debris; invisible water pollutants sometimes can be much more harmful than visible ones. *Source: Stephen Codrington at Wikimedia Commons*

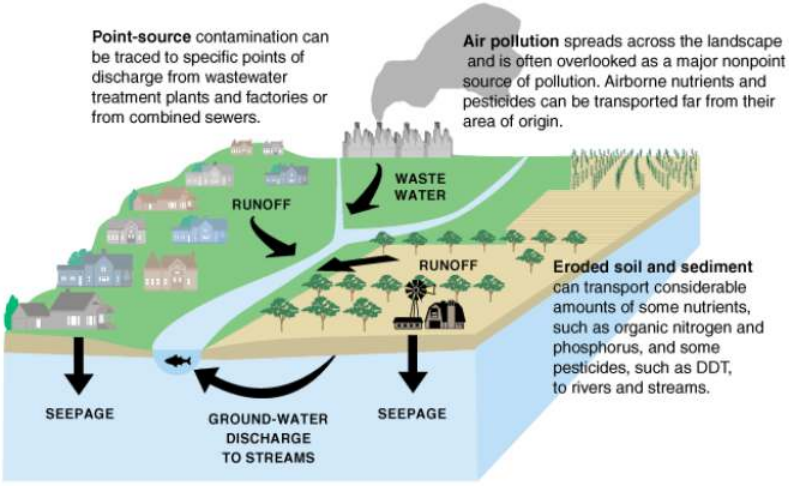


Figure 10.3.2.7 Sources of Water Contamination. Sources of some water pollutants and movement of pollutants into different water reservoirs of the water cycle. *Source: U.S. Geological Survey*

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. Point sources of pollution include animal "factory" farms that raise a large number and high density of livestock such as cows, pigs, and chickens (see Figure 10.3.2.8) and discharge 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 into surface waters (see Figure 10.3.2.9). Nonpoint sources of pollution include agricultural fields, cities, and abandoned mines. Rainfall runs over the land and through the ground, picking up pollutants such as herbicides, pesticides, and fertilizer from agricultural fields and lawns; oil, antifreeze, car detergent, animal waste, and road salt from urban areas; and acid and toxic elements from abandoned mines. Then, this pollution is carried into surface water bodies and groundwater. Nonpoint source pollution, which is the leading cause of water pollution in the U.S., is

usually much more difficult and expensive to control than point source pollution because of its low concentration, multiple sources, and much greater volume of water.



Figure 10.3.2.8 A Commercial Meat Chicken Production House. This chicken factory farm is a possible major point source of water pollution. *Source: Larry Rana at Wikimedia Commons*

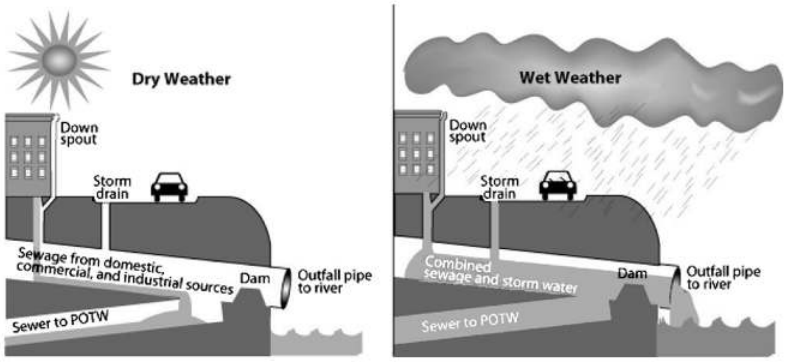


Figure 10.3.2.9 Combined Sewer System. A combined sewer system is a possible major point source of water pollution during heavy rain due to overflow of untreated sewage. During dry weather (and small storms), all flows are handled by the publicly owned treatment works (POTW). During large storms, the relief structure allows some of the combined stormwater and sewage to be discharged untreated to an adjacent water body. *Source: U.S. Environmental Protection Agency at Wikimedia Commons*

Types of Water Pollutants

Oxyden-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 (chemically represented in a simplified way as CH_2O) and remove dissolved oxygen (O_2) according to the following reaction:

$$CH2O + O2 \rightarrow CO2 + H2O$$

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 most natural waters is sewage; grass and leaves are smaller sources. An unpolluted water body with respect to oxygen 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, e.g., bass, trout, and perch dominate. 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, e.g., 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*, 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 P-based detergent) can cause cultural eutrophication, which involves the rapid growth of aquatic plants, particularly algae, called an *algal bloom*. Thick mats of floating and rooted green or sometimes red algae (see Figure **10.3.2.10**) create water pollution, damage the ecosystem by clogging fish gills and blocking sunlight, and damage lake aesthetics by making recreation difficult and creating an eyesore. A small percentage of algal species produce toxins that can kill fish, mammals, and birds, and may cause human illness; explosive growths of these algae are called *harmful algal blooms* (see Figure **10.3.2.11**). When the prolific algal layer dies, it becomes oxygen-demanding waste, which can create very low O_2 water (<~2 ppm O_2), called hypoxia or dead zone because it causes death 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 (see Figure **10.3.2.12**), 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.



Figure **10.3.2.10** Algal Bloom in River in Sichuan, China. Algal blooms can present problems for ecosystems and human society. *Source: Felix Andrews via Wikimedia Commons*



Figure **10.3.2.11** Harmful Algal Bloom. Harmful algal bloom with deep red color. *Source: Kai Schumann via National Oceanic and Atmospheric Administration*

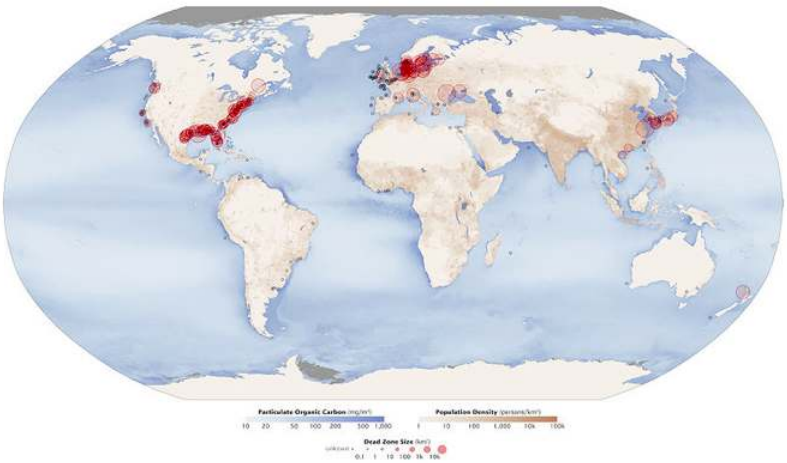


Figure **10.3.2.12** Aquatic Dead Zones. Zones of hypoxia shown as red circles. Black dots show hypoxia zones of unknown size, brown shading shows population density, and blue shading shows density of particulate organic carbon, an indicator of organic productivity. *Source: Robert Simmon & Jesse Allen at NASA Earth Observatory via Wikimedia Commons*

Pathogens are disease-causing microorganisms, e.g., viruses, bacteria, parasitic worms, and protozoa, which cause a variety of intestinal diseases such as dysentery, typhoid fever, hepatitis, and cholera. Pathogens are the major cause of the water pollution crisis discussed at the beginning of this section. Unfortunately nearly a billion people around the world are exposed to waterborne pathogen pollution daily and around 1.5 million children mainly in underdeveloped countries die every year of waterborne diseases from pathogens (see Figure **10.3.2.3**). Pathogens enter water primarily from human and animal fecal waste due to inadequate sewage treatment. In many underdeveloped countries, sewage is discharged into local waters either untreated or after only rudimentary treatment. In developed countries untreated sewage discharge can occur from overflows of combined sewer systems, poorly managed livestock factory farms, and leaky or broken sewage collection systems (see Figure **10.3.2.14**). Water with pathogens can be remediated by adding chlorine or ozone, by boiling, or by treating the sewage in the first place.



Figure **10.3.2.13** Overflowing Sanitary Sewer. A manhole cover blown off by a June 2006 sanitary sewer overflow in Rhode Island. *Source: U.S. Environmental Protection Agency via Wikimedia Commons*

Oil spills are another kind of organic pollution. Oil spills can result from supertanker accidents such as the Exxon Valdez in 1989, which spilled 10 million gallons of oil into the rich ecosystem of offshore south Alaska and killed massive numbers of animals. The largest marine oil spill was the Deepwater Horizon disaster, which began with a natural gas explosion (see Figure **10.3.2.14**) at an oil well 65 km offshore of Louisiana and flowed for 3 months in 2010, releasing an estimated 200 million gallons of oil. The worst oil spill ever occurred during the Persian Gulf war of 1991, when Iraq deliberately dumped approximately 200 million gallons of oil in offshore Kuwait and set more than 700 oil well fires that released enormous clouds of smoke and acid rain for over nine months. During an oil spill on water, oil floats to the surface because it is less dense than water, and the lightest hydrocarbons evaporate, decreasing the size of the spill but polluting the air. Then, bacteria begin to decompose the remaining oil, in a process that can take many years. After several months only about 15% of the original volume may remain, but it is in thick asphalt lumps, a form that is particularly harmful to birds, fish, and shellfish. Cleanup operations can include *skimmer ships* that vacuum oil from the water surface (effective only for small spills), controlled *burning* (works only in early stages before the light, ignitable part evaporates but also pollutes the air), *dispersants* (detergents that break up oil to accelerate its decomposition, but some dispersants may be toxic to the ecosystem), and *bioremediation* (adding microorganisms that specialize in quickly decomposing oil, but this can disrupt the natural ecosystem).



Figure **10.3.2.14** Deepwater Horizon Explosion. Boats fighting the fire from an explosion at the Deepwater Horizon drilling rig in Gulf of Mexico offshore Louisiana on April 20, 2010. *Source: United States Coast Guard via Wikimedia Commons*

Toxic chemicals involve many different kinds and sources, primarily from industry and mining. General kinds of toxic chemicals include *hazardous chemicals*, which are a wide variety of synthetic organic and inorganic chemicals such as acids, bases, cyanide,

and a class of compounds called persistent organic pollutants that includes *DDT* (pesticide), *dioxin* (herbicide by-product), and *PCBs* (polychlorinated biphenyls, which were used as a liquid insulator in electric transformers). Persistent organic pollutants are long-lived in the environment, accumulate through the food chain (bioaccumulation), and can be toxic. Another category of toxic chemicals includes *radioactive materials* such as cesium, iodine, uranium, and radon gas, which can result in long-term exposure to radioactivity if it gets into the body. A final group of toxic chemicals is heavy metals such as lead, mercury, arsenic, cadmium, and chromium, which can accumulate through the food chain. Heavy metals are commonly produced by industry and at metallic ore mines. Arsenic and mercury are discussed in more detail below. The US EPA regulates 83 contaminants in drinking water to ensure a safe public water supply. Similarly, at the international level the World Health Organization has drinking water standards for a variety of contaminants.

Arsenic (As) has been famous as an agent of death for many centuries. In large doses arsenic causes cancer and can be fatal. Only recently have scientists recognized that health problems can be caused by drinking small arsenic concentrations in water over a long time. It attacks the central nervous system and can damage the respiratory system, bladder, lungs, liver, and kidneys. It enters the water supply naturally from weathering of As-rich minerals and from human activities such as coal burning and smelting of metallic ores. The worst case of arsenic poisoning occurred in the densely populated impoverished country of Bangladesh, which had experienced 100,000s of deaths from diarrhea and cholera each year from drinking surface water contaminated with pathogens due to improper sewage treatment. In the 1970s the United Nations provided aid for millions of shallow water wells, which resulted in a dramatic drop in pathogenic diseases. Unfortunately, many of the wells produced water naturally rich in arsenic. Tragically, there are an estimated 77 million people (about half of the population) who inadvertently may have been exposed to toxic levels of arsenic in Bangladesh as a result. The World Health Organization has called it the largest mass poisoning of a population in history.

Mercury (Hg) is used in a variety of electrical products, such as dry cell batteries, fluorescent light bulbs, and switches, as well as in the manufacture of paint, paper, vinyl chloride, and fungicides. In the methylmercury form (CH_3Hg^+) it is highly toxic; ≥ 1 ppb of methylmercury represents water contaminated with mercury. Mercury concentrates in the food chain, especially in fish, in a process caused biomagnification (see Sidebar Biomagnification). It acts on the central nervous system and can cause loss of sight, feeling, and hearing as well as nervousness, shakiness, and death. Like arsenic, mercury enters the water supply naturally from weathering of Hg-rich minerals and from human activities such as coal burning and metal processing. A famous mercury poisoning case in Minamata, Japan involved methylmercury-rich industrial discharge that caused high Hg levels in fish. People in the local fishing villages ate fish up to three times per day for over 30 years, which resulted in over 2,000 deaths. During that time the responsible company and national government did little to mitigate, help alleviate, or even acknowledge the problem.

Biomagnification

Biomagnification represents the processes in an ecosystem that cause greater concentrations of a chemical, such as methylmercury, in organisms higher up the food chain. Mercury and methylmercury are present in only very small concentrations in seawater; however, at the base of the food chain algae absorb methylmercury. Then, small fish eat the algae, large fish and other organisms higher in the food chain eat the small fish, and so on. Fish and other aquatic organisms absorb methylmercury rapidly but eliminate it slowly from the body. Therefore, each step up the food chain increases the concentration from the step below (see Figure **10.3.2.15**). Largemouth bass can concentrate methylmercury up to 10 million times over the water concentration and fish-eating birds can concentrate it even higher. Other chemicals that exhibit biomagnification are DDT, PCBs, and arsenic.



Figure **10.3.2.15** An illustrative example of biomagnification of mercury from water through the food chain and into a bird's egg. *Source:* U.S. Geological Survey

Other water pollutants include sediment and heat. Muddy water is bad for drinking but even worse for underwater plants that need sunlight for photosynthesis. Much of the sediment in water bodies is derived from the erosion of soil, so it also represents a loss of agricultural productivity. Thermal pollution involves the release of heated waters from power plants and industry to surface water, causing a drop in the dissolved O_2 content, which can stress fish.

Hard water contains abundant calcium and magnesium, which reduces its ability to develop soapsuds and enhances *scale* (calcium and magnesium carbonate minerals) formation on hot water equipment. Water softeners remove calcium and magnesium, which allows the water to lather easily and resist scale formation. Hard water develops naturally from the dissolution of calcium and magnesium carbonate minerals in soil; it does not have negative health effects in people.

Groundwater pollution can occur from underground sources and all of the pollution sources that contaminate surface waters. Common sources of groundwater pollution are leaking underground storage tanks for fuel, septic tanks, agricultural activity, and landfills. Common groundwater pollutants include nitrate, pesticides, volatile organic compounds, and petroleum products. Polluted groundwater can be a more serious problem than polluted surface water because the pollution in groundwater may go undetected for a long time because usually it moves very slowly. As a result, the pollution in groundwater may create a contaminant plume, a large body of flowing polluted groundwater (see Figure **10.3.2.15**), making cleanup very costly. By the time groundwater contamination is detected, the entity responsible for the pollution may be bankrupt or nonexistent. Another troublesome feature of groundwater pollution is that small amounts of certain pollutants, e.g., petroleum products and organic solvents, can contaminate large areas. In Denver, Colorado 80 liters of several organic solvents contaminated 4.5 trillion liters of groundwater and produced a 5 km long contaminant plume. Most groundwater contamination occurs in shallow, unconfined aquifers located near the contamination source. Confined aquifers are less susceptible to pollution from the surface because of protection by the confining layer. A major threat to groundwater quality is from underground fuel storage tanks. Fuel tanks commonly are stored underground at gas stations to reduce explosion hazards. Before 1988 in the U.S. these storage tanks could be made of metal, which can corrode, leak, and quickly contaminate local groundwater. Now, leak detectors are required and the metal storage tanks are supposed to be protected from corrosion or replaced with fiberglass tanks. Currently there are around 600,000 underground fuel storage tanks in the U.S. and over 30% still do not comply with EPA regulations regarding either release prevention or leak detection.

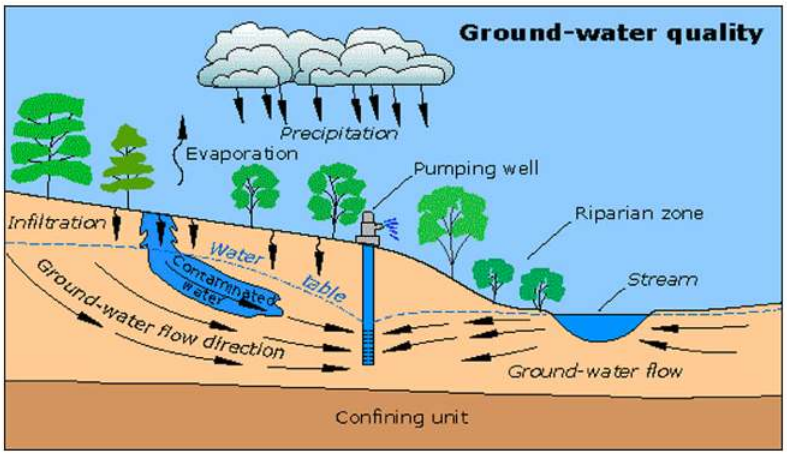


Figure **10.3.2.16** Contaminant Plume in Groundwater. Mapping how a contaminant plume will migrate once it reaches groundwater requires understanding of the pollutant's chemical properties, local soil characteristics, and how permeable the aquifer is. *Source: United States Geological Survey*

Sustainable Solutions to the Water Pollution Crisis?

Resolution of the global water pollution crisis described at the beginning of this section requires multiple approaches to improve the quality of our fresh water and move towards sustainability. The most deadly form of water pollution, pathogenic microorganisms that cause waterborne diseases, kills almost 2 million people in underdeveloped countries every year. The best strategy for addressing this problem is proper sewage (wastewater) treatment. Untreated sewage is not only a major cause of pathogenic diseases, but also a major source of other pollutants, including oxygen-demanding waste, plant nutrients (N and P), and toxic heavy metals. Wastewater treatment is done at a sewage treatment plant in urban areas and through a septic tank system in rural areas.

The main purpose of a sewage treatment plant is to remove organic matter (oxygen-demanding waste) and kill bacteria; special methods also can be used to remove plant nutrients and other pollutants. The numerous processing steps at a conventional sewage treatment plant (see Figure **10.3.2.17**) include *pretreatment* (screening and removal of sand and gravel), *primary treatment* (settling or floatation to remove organic solids, fat, and grease), *secondary treatment* (aerobic bacterial decomposition of organic solids), *tertiary treatment* (bacterial decomposition of nutrients and filtration), *disinfection* (treatment with chlorine, ozone, ultraviolet light, or bleach), and either *discharge* to surface waters (usually a local river) or *reuse* for some other purpose, such as irrigation, habitat preservation, and artificial groundwater recharge. The concentrated organic solid produced during primary and secondarytreatment is called sludge, which is treated in a variety of ways including landfill disposal, incineration, use as fertilizer, and anaerobic

bacterial decomposition, which is done in the absence of oxygen. Anaerobic decomposition of sludge produces methane gas, which can be used as an energy source. To reduce water pollution problems, separate sewer systems (where street runoff goes to rivers and only wastewater goes to a wastewater treatment plant) are much better than combined sewer systems, which can overflow and release untreated sewage into surface waters during heavy rain. Some cities such as Chicago, Illinois have constructed large underground caverns and also use abandoned rock quarries to hold storm sewer overflow. After the rain stops, the stored water goes to the sewage treatment plant for processing.

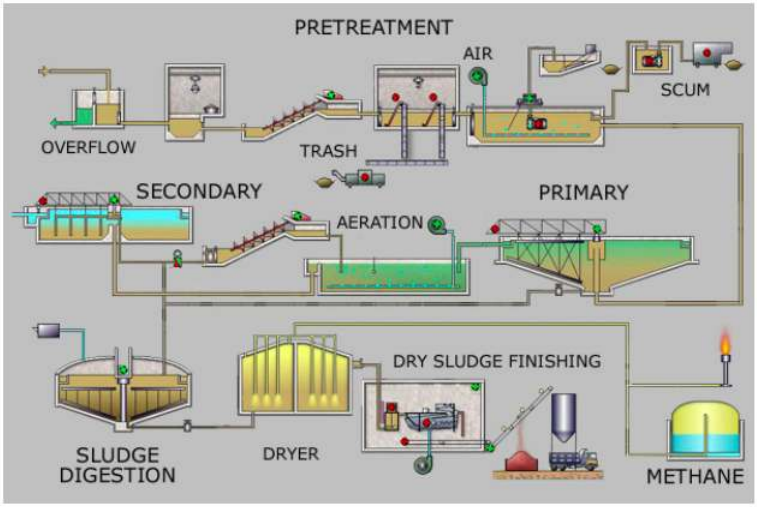


Figure **10.3.2.17** Steps at a Sewage Treatment Plant. The numerous processing steps at a conventional sewage treatment plant include pretreatment (screening and removal of sand and gravel), primary treatment (settling or floatation to remove organic solids, fat, and grease), secondary treatment (aerobic bacterial decomposition of organic solids), tertiary treatment (bacterial decomposition of nutrients and filtration), disinfection (treatment with chlorine, ozone, ultraviolet light, or bleach), and either discharge to surface waters (usually a local river) or reuse for some other purpose, such as irrigation, habitat preservation, and artificial groundwater recharge. *Source: Leonard G.via Wikipedia*

A septic tank system is an individual sewage treatment system for homes in rural and even some urban settings. The basic components of a septic tank system (see Figure **10.3.2.18**) include a sewer line from the house, a *septic tank* (a large container where sludge settles to the bottom and microorganisms decompose the organic solids anaerobically), and the drain field (network of perforated pipes where the clarified water seeps into the soil and is further purified by bacteria). Water pollution problems occur if the septic tank malfunctions, which usually occurs when a system is established in the wrong type of soil or maintained poorly.

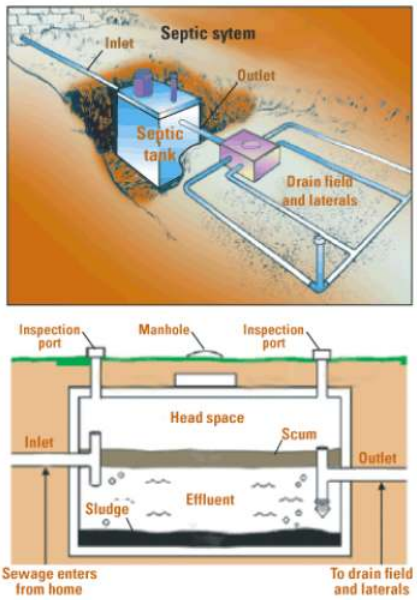


Figure **10.3.2.18** Septic System. Septic tank system for sewage treatment. *Source: United States Geological Survey*

For many developing countries, financial aid is necessary to build adequate sewage treatment facilities; however, the World Health Organization estimates an estimated cost savings of between $3 and $34 for every $1 invested in clean water delivery and sanitation (Water for Life, 2005). The cost savings are from health care savings, gains in work and school productivity, and deaths prevented. Simple and inexpensive techniques for treating water at home include chlorination, filters, and solar disinfection. Another alternative is to use constructed wetlands technology (marshes built to treat contaminated water), which is simpler and cheaper than a conventional sewage treatment plant.

Bottled water is *not* a sustainable solution to the water crisis, despite exponential growth in popularity in the U.S. and the world. Bottled water is not necessarily any safer than the U.S. public water supply, it costs on average about 700 times more than U.S. tap water, and every year it uses approximately 200 billion plastic and glass bottles that have a relatively low rate of recycling. Compared to tap water, it uses much more energy, mainly in bottle manufacturing and long-distance transportation. If you don't like the taste of your tap water, then please use a water filter instead of bottled water!



Figure **10.3.2.19** Storm Drain. Curbside storm drain receiving urban runoff. *Source: By Robert Lawton via Wikimedia Commons*

Additional sustainable solutions to the water pollution crisis include legislation to eliminate or greatly reduce point sources of water pollution. In the U.S., the Clean Water Act of 1972 and later amendments led to major improvements in water quality (see Sidebar Clean Water Act). Nonpoint sources of water pollution, e.g., agricultural runoff and urban runoff (see Figure **10.3.2.19**), are much harder to regulate because of their widespread, diffuse nature. There are many construction and agricultural practices that reduce polluted runoff including no-till farming and sediment traps. Artificial aeration or mechanical mixing can remediate lakes with oxygen depletion. Specific things that we can do to reduce urban runoff include the following: keep soil, leaves, and grass clippings off driveways, sidewalks, and streets; don't pour used motor oil, antifreeze, paints, pesticides, or any household hazardous chemical down the storm sewer or drain; recycle used motor oil; use hazardous waste disposal programs offered by the community; compost your organic waste; don't use fertilizers and herbicides on your lawn; and flush pet waste down the toilet.

Clean Water Act

During the early 1900s rapid industrialization in the U.S. resulted in widespread water pollution due to free discharge of waste into surface waters. The Cuyahoga River in northeast Ohio caught fire numerous times (see Figure **10.3.2.20**), including a famous fire in 1969 that caught the nation's attention. In 1972 Congress passed one of the most important environmental laws in U.S. history, the Federal Water Pollution Control Act, which is more commonly called the Clean Water Act. The purpose of the Clean Water Act and later amendments is to maintain and restore water quality, or in simpler terms to make our water swimmable and fishable. It became illegal to dump pollution into surface water unless there was formal permission and U.S. water quality improved significantly as a result. More progress is needed because currently the EPA considers over 40,000 U.S. water bodies as impaired, most commonly due to pathogens, metals, plant nutrients, and oxygen depletion. Another concern is protecting groundwater quality, which is not yet addressed sufficiently by federal law.


Figure 10.3.2.20 Cuyahoga River on Fire. *Source:* National Oceanic and Atmospheric

Sometimes slow flow through a soil can naturally purify groundwater because some pollutants, such as P, pesticides, and heavy metals, chemically bind with surfaces of soil clays and iron oxides. Other pollutants are not retained by soil particles: These include N, road salt, gasoline fuel, the herbicide atrazine, tetrachloroethylene (a carcinogenic cleaning solvent used in dry cleaning), and vinyl chloride. In other cases, slow groundwater flow can allow bacteria to decompose dead organic matter and certain pesticides. There are many other ways to remediate polluted groundwater. Sometimes the best solution is to stop the pollution source and allow natural cleanup. Specific treatment methods depend on the geology, hydrology, and pollutant because some light contaminants flow on top of groundwater, others dissolve and flow with groundwater, and dense contaminants can sink below groundwater. A common cleanup method called pump and treat involves pumping out the contaminated groundwater and treating it by oxidation, filtration, or biological methods. Sometimes soil must be excavated and sent to a landfill. In-situ treatment methods include adding chemicals to immobilize heavy metals, creating a permeable reaction zone with metallic iron that can destroy organic solvents, or using bioremediation by adding oxygen or nutrients to stimulate growth of microorganisms.

Review Questions

1. What are the major kinds of water pollutants and how do they degrade water quality?
2. How would you rank the water pollution problems described in this chapter? Why?
3. Why is untreated sewage such an important water pollutant to remediate?
4. What should society learn from the case history of Love Canal?
5. Why are people facing a crisis involving water pollution and how can we solve it?

References

Water for Life: Making it Happen (2005) World Health Organization and UNICEF. Retrieved from http://www.who.int/water_sanitation_health/waterforlife.pdf

World Health Statistics (2010) World Health Organization. Retrieved from http://www.who.int/whosis/whostat/EN_WHS10_Full.pdf

Glossary

arsenic

A type of water pollutant that can be fatal in large doses and can cause health problems in small doses over a long time.

biochemical oxygen demand

The amount of oxygen used by aerobic (in presence of oxygen) bacterial decomposition of organic matter.

bioremediation

Method of groundwater remediation involving the addition oxygen or nutrients. to stimulate growth of microorganisms, which decompose an organic pollutant.

bottled water

Drinking water packaged in plastic bottles or glass bottles, bottled water is not a sustainable solution to the water crisis because of the nonrenewable energy and material resources involved in manufacturing and transporting it.

combined sewer systems

A single set of underground pipes used to collect both sewage and. storm water runoff from streets for wastewater treatment.

constructed wetland

Marsh built to treat contaminated water.

contaminant plume

A large body of flowing polluted groundwater.

cultural eutrophication

Rapid aquatic plant growth, particularly algae, in a surface water body.

excessive plant nutrient

A type of water pollutant involving a limiting plant nutrient that usually is present in water at low concentrations and therefore restricts the total amount of plant growth, examples include nitrogen and phosphorous.

hard water

Water with abundant calcium and magnesium, which reduces its ability to develop soapsuds and enhances scale; hard water does not have negative health effects in people.

heat

A type of water pollutant that causes a drop in the dissolved oxygen content, which can stress fish.

heavy metal

A type of water pollutant involving elements such as lead, mercury, arsenic, cadmium, and chromium, which can accumulate through the food chain.

hypoxia

Very low oxygen water due to prolific growth of algae, algal death, and then decomposition, also called dead zone.

mercury

A type of water pollutant that acts on the central nervous system and can cause loss of sight, feeling, and hearing as well as nervousness, shakiness, and death.

nonpoint source (of water pollution)

Large and diffuse location where a pollution source occurs.

oil spill

A type of organic water pollutant involving the release of liquid petroleum into the environment due to human activity.

oxygen-demanding waste

A type of water pollutant involving abundant dead organic matter.

pathogens

Disease-causing microorganisms, e.g., viruses, bacteria, parasitic worms, and protozoa, which cause a variety of intestinal diseases such as dysentery, typhoid fever, hepatitis, and cholera.

persistent organic pollutant

A group of organic water pollutants that are long-lived in the environment, accumulate through the food chain, and can be toxic.

point source (of water pollution)

Readily identifiable and relatively small location where a pollution source occurs.

sediment

A type of water pollutant that degrades drinking water and can kill underwater plants that need sunlight for photosynthesis.

septic tank system

An individual sewage treatment system for homes in rural and even some urban settings.

sewage treatment plant

A facility that processes wastewater with the main goal of removing organic matter (oxygen-demanding waste) and killing bacteria.

sludge

Concentrated organic solid produced during primary and secondarytreatment of sewage treatment.

solvent

Capacity of a liquid such as water to dissolve soluble minerals.

total dissolved solids

Total amount of dissolved material in water, typically reported in parts per million (ppm) units.

toxic chemical

A type of organic water pollutant involving chemicals with a severe human health risk.

underground fuel storage tank

A type of water pollutant if it leaks.

water pollution

Contamination of water by an excess amount of a substance that can cause harm to human beings and the ecosystem.

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10.3.3: Biological Contamination of Water

Learning Objectives

- Identify the three categories of pathogens that produce water-borne diseases.
- Provide one example of each pathogen, typical sources, and health problems.
- Summarize how water-borne diseases can be prevented and treated.
- Recall areas of the world where water is not properly sanitized.
- List foods and beverages that need to be avoided when using water that is not sanitized.
- Recall how long to boil water if under an advisory.
- Realize that boiling does not remove inorganics, metals, or organics.
- Besides boiling, discuss the chemical sanitation process of how to sanitize water at home (EPA method below).

Water Borne Diseases

If water is not cleaned properly, residents of a community can contract various illnesses. Viruses, bacteria, and parasites can enter a water supply unknowingly. All three of these species are pathogenic, or disease-causing. In the United States, the Environmental Protection Agency (EPA) quantifies and monitors these pathogens in water systems that serve at least 200 consumers. The EPA classifies these contaminants as being microorganisms (even though a biologist might dispute this terminology).



Video **10.3.3.1**: 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

Approximately 829,000 people die each year due to developing diarrheal illnesses from water based illnesses. Of the number, over 297,000 of these fatalities are children under five years of age. From a worldwide perspective, 785 million lack access to an improved water source. That is, this large group of people do not extract their water from a household connection, public standpipe, borehole/protected well, protected spring, or rainwater collection. Implementing water sanitation and hygiene for people who live in these countries could prevent at least 9.1% of the global disease burden and 6.3% of all deaths.



Figure 10.3.3.1:This young girl was collecting water from a sacred pond in Ogi, Nigeria, but she won't get Guinea worm because the water had been treated, and steps had been installed, so people couldn't contaminate the water. Creator: CDC/ The Carter Center. (Copyright, Public Health Library).

One of the many waterborne pathogens that can be contracted by drinking unclean water is Giardiasis. The picture below 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.

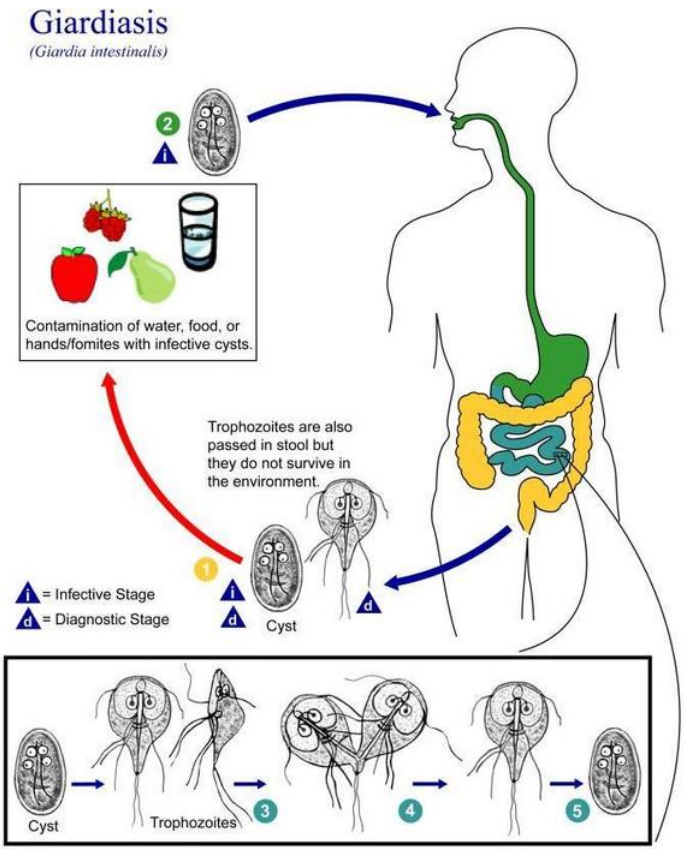


Figure 10.3.3.2: The life cycle of Giardia.

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 **10.3.3.1**: 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

When traveling to places that do not have comprehensive water sanitation procedures, it is important to avoid certain foods and beverages. Ice and tap water should be avoided to reduce risk of exposure to pathogens. In addition, vegetables and fruits that do not have a peel could cause water borne illness. If possible, purchase bottled water from a reputable company (Nestle is common in Asia and South America)



Center for Disease Control (CDC) Sanitizing Information

Water advisories may be declared if sanitation is compromised. In these situations, boiling, halogen disinfection, or filtration could be utilized to make water **potable** (drinkable). The Centers for Disease Control has developed a document to compare these different methods of sanitation. Look below to see the most effective ways to make water safe.

This document should only serve as a guide for individuals intending to use untreated or poorly treated water as a drinking water source. This document may also aid travelers and backcountry water users in researching drinking water treatment methods. Except for boiling, few of the water treatment methods are 100% effective in removing all pathogens.

Table Key for Pathogen Removal	
-	not effective
+	low effectiveness
++	moderate effectiveness
+++	high effectiveness
++++	very high effectiveness

Contaminant	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water	Methods that may remove some/all of the contaminant				
			REMEMBER: If boiling water is not a feasible option, the most effective pathogen reduction method in untreated or poorly treated drinking water is a combination treatment, using the appropriate filtration and disinfection methods.				
			Boiling (Rolling boil for 1 minute minimum) *	Filtration **	Disinfection***		Combination Filtration and Disinfection****
					Iodine or Chlorine	Chlorine Dioxide	
Protozoa- ***Cryptosporidium***	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste	++++	+++ Absolute ≤ 1.0 micron filter (NSF Standard 53 or 58 rated "cyst reduction / removal" filter)	–	+ to ++	++++ Absolute ≤ 1.0 micron filter (NSF Standard 53 or 58 rated "cyst reduction / removal" filter)
Protozoa- ***Giardia intestinalis*** **(aka** ***Giardia lamblia*****)**	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste	++++	+++ Absolute ≤ 1.0 micron filter (NSF Standard 53 or 58 rated "cyst reduction / removal" filter)	+ to ++	+++	++++ Absolute ≤ 1.0 micron filter (NSF Standard 53 or 58 rated "cyst reduction / removal" filter)
Bacteria- **(e.g.,** ***Campylobacter, Salmonella, Shigella, E. coli*****)**	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste	++++	++ Absolute ≤ 0.3 micron filter	+++	+++	++++ Absolute ≤ 0.3 micron filter
Viruses- **(e.g., enterovirus, hepatitis A, norovirus, rotavirus)**	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste	++++	–	+++	+++	+++

Treatment methods listed above:

* **Boiling** can be used as a pathogen reduction method that should kill all pathogens. Water should be brought to a rolling boil for 1 minute (at altitudes greater than 6,562 feet (>2,000 m), boil water for 3 minutes.)

** **Filtration** can be used as a pathogen reduction method against most microorganisms, depending on the pore size of the filter, amount of the contaminant, particle size of the contaminant, and charge of the contaminant particle. Manufacturer's instructions must be followed. More information on selecting an appropriate water filter can be found at www.cdc.gov/crypto/factsheets/filters.html. Only filters that contain a chemical disinfectant matrix will be effective against some viruses.

*** **Disinfection** can be used as a pathogen reduction method against microorganisms. However, contact time, disinfectant concentration, water temperature, water turbidity (cloudiness), water pH, and many other factors can impact the effectiveness of chemical disinfection. The length of time and concentration of disinfectant varies by manufacturer and effectiveness of pathogen reduction depends on the product. Depending on these factors, 100% effectiveness may not be achieved. Manufacturer's instructions must be followed.

**** If boiling water is not possible, a **Combination of Filtration and Chemical Disinfection** is the most effective pathogen reduction method in drinking water for backcountry or travel use. Manufacturer's instructions must be followed.

Other treatment methods can be effective against some of the above pathogens:

- **Ultraviolet Light (UV Light)** can be used as a pathogen reduction method against some microorganisms. The technology requires effective prefiltering due to its dependence on low water turbidity (cloudiness), the correct power delivery, and correct contact times to achieve maximum pathogen reduction. UV might be an effective method for pathogen reduction in untreated or poorly treated water; there is a lack of independent testing data available on specific systems. Manufacturer's instructions must be followed.
- **MIOX®** systems use a salt solution to create mixed oxidants, primarily chlorine. As a result, refer to the category above for chlorine disinfection. Manufacturer's instructions must be followed.

Important: Water that has been disinfected with iodine is **NOT** recommended for pregnant women, people with thyroid problems, those with known hypersensitivity to iodine, or continuous use for more than a few weeks at a time.

In addition to using the appropriate drinking water treatment methods listed above, you can also protect yourself and others from waterborne illness by:

- **Burying human waste 8 inches deep and at least 200 feet away from natural waters.**
- **Practicing good personal hygiene. Wash hands before handling food, eating, and after using the toilet.**

Halogen based solids can be purchased at most home improvement stores, pool stores, Walmart, and Target. These chemicals will alter taste and smell of water. These chemicals are also needed when properly sanitizing a pool or a hot tub. Halogen tablets are quite cheap and an effective way for sanitizing any type of water.

EPA: EMERGENCY DISINFECTION OF DRINKING WATER

In an emergency situation where regular water service has been interrupted – like a hurricane, flood, or water pipe breakage – local authorities may recommend using only bottled water, boiled water, or disinfected water until regular water service is restored. The instructions below show you how to boil and disinfect water to kill most disease-causing microorganisms that may be present in the water. However, boiling or disinfection will not destroy other contaminants, such as heavy metals, salts, and most other chemicals.

> *ONLY USE WATER THAT HAS BEEN PROPERLY DISINFECTED FOR DRINKING, COOKING, MAKING ANY PREPARED DRINK, WASHING DISHES, AND FOR BRUSHING TEETH.*

Use **bottled wate**r or water you have properly prepared and stored as an emergency water supply.

Boil water, if you do not have bottled water. Boiling is sufficient to kill pathogenic bacteria, viruses and protozoa (WHO, 2015).

- If water is cloudy, let it settle and filter it through a clean cloth, paper towel, or coffee filter.
- Bring water to a rolling boil for at least one minute. At altitudes above 5,000 feet (1,000 meters), boil water for three minutes.
- Let the water cool naturally and store it in clean containers with covers.
- To improve the flat taste of boiled water, add one pinch of salt to each quart or liter of water, or pour the water from one clean container to another several times.

Disinfect water using household bleach, if you can't boil water. Only use regular, unscented chlorine bleach products that are suitable for disinfection and sanitization as indicated on the label. The label may say that the active ingredient contains 6 or 8.25% of sodium hypochlorite. Do not use scented, color safe, or bleaches with added cleaners.

- If water is cloudy, let it settle and filter it through a clean cloth, paper towel, or coffee filter.
- Locate a clean dropper from your medicine cabinet or emergency supply kit.
- Locate a fresh liquid chlorine bleach or liquid chlorine bleach that is stored at room temperatures for less than one year.
- Use the table on the next page as a guide to decide how much bleach you should add to the water, for example, add 8 drops of 6 % bleach or 6 drops of 8.25% bleach to each gallon of water. Double the amount of bleach if the water is cloudy, colored, or very cold.
- Stir and let stand for 30 minutes. The water should have a slight chlorine odor. If it doesn't, repeat the dosage and let stand for another 15 minutes before use.
- If the chlorine taste is too strong, pour the water from one clean container to another and let it stand for a few hours before use.

Volume of Water	Amount of 6% Bleach to Add†	Amount of 8.25% Bleach to Add†
1 quart/liter	2 drops	2 drops
1 gallon	8 drops	6 drops
2 gallons	16 drops (1/4 tsp.)	12 drops (1/4 tsp.)
4 gallons	1/3 tsp.	1/4 tsp.
8 gallons	2/3 tsp.	1/2 tsp.

†Bleach may contain 6 or 8.25% sodium hypochlorite

ADDITIONAL WATER GUIDANCE FOR EMERGENCIES

Prepare and store an emergency water supply. Visit the Federal Emergency Management Agency (FEMA) website for additional guidance on preparing and storing an emergency water supply.

Look for other sources of water in and around your home. Although bottled water is your best choice, you may be able to find other sources of water by melting ice cubes or draining your hot water tank or pipes. You can also use river or lake water. It is generally better to use flowing water than still, stagnant water. However, do not use water with floating material in it or water that has a dark color or questionable odor. Regardless of the source, treat the water by following the instructions above. If you have a well on your property that has been flooded, make sure to disinfect and test the well water after the flood. Contact your state or local health department for advice or go here.

Consider how the water looks and how to filter it if needed. Disinfection does not work as well when water is cloudy or colored. If water is cloudy, let it settle. Then filter the water through a clean cloth, paper towel, or coffee filter. Store the settled and filtered water in clean containers with covers

OTHER DISINFECTION METHODS

If you don't have liquid bleach, you can use one of the other disinfection methods described below.

- *Granular calcium hypochlorite*. The first step is to make a chlorine solution that you will use to disinfect your water. For your safety, do it in a ventilated area and wear eye protection. Add one heaping teaspoon (approximately ¼ ounce) of high-test granular calcium hypochlorite (HTH) to two gallons of water and stir until the particles have dissolved. The mixture will produce a chlorine solution of approximately 500 milligrams per liter. To disinfect water, add one part of the chlorine solution to every 100 parts of water you are treating. This is about the same as adding 1 pint (16 ounces) of the chlorine solution to 12.5 gallons of water. If the chlorine taste is too strong, pour the water from one clean container to another and let it stand for a few hours before use. CAUTION: HTH is a very powerful oxidant. Follow the instructions on the label for safe handling and storage of this chemical.
- *Common household iodine* (or "tincture of iodine"). You may have iodine in your medicine cabinet or first aid kit. Add five drops of 2% tincture of iodine to each quart or liter of water that you are disinfecting. If the water is cloudy or colored, add 10 drops of iodine. Stir and let the water stand for at least 30 minutes before use.
- *Water disinfection tablets*. You can disinfect water with tablets that contain chlorine, iodine, chlorine dioxide, or other disinfecting agents. These tablets are available online or at pharmacies and sporting goods stores. Follow the instructions on the product label as each product may have a different strength.

Safe Drinking Water Hotline: 1-800-426-4791 water.epa.gov/drink/hotline

Example 10.3.3.1

1. Do all waterborne pathogens cause stomach illnesses?
2. If your community is under a water advisory, then how long should you boil tap water to kill pathogens?
3. Vaccinations and preventive medications can protect you from which pathogens?
4. When properly diluted, which common household cleaner can sanitize tap water?

Answer

1. Legionella bacteria causes respiratory problems. Also, hepatitis and polio viruses do not produce stomach illnesses.
2. Water should be boiled rigorously for at least one minute to kill most pathogens.
3. Vaccines can be used to prevent: hepatitis, typhoid, cholera, and polio. In the United States, most children have been vaccinated from hepatitis and polio. When traveling to destinations that lack sanitized water, it would be beneficial to request prescription medications from your health care professional. Refer to the chart above regarding which diseases can be treated with medications.
4. A diluted (watered down) form of bleach (sodium hypochlorite) can be used to sanitize water. Please note the different types of bleach that can be purchased. In addition, do not use color safe or scented bleach.

References

1. World Health Organization. Drinking-water (who.int)
2. The Center For Disease Control. Global WASH Fast Facts | Global Water, Sanitation and Hygiene | Healthy Water | CDC

Contributors and Attributions

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10.3.4: Chemical Contamination of Water

Learning Objectives

- Realize how combustion processes affect water sources.
- Define the pH and composition of acid rain (three specific formulas/names).
- Know the precursors of acid rain.
- Recall the environmental and biological effects of acid rain.
- Understand the differences between hard and soft water.
- Connect inorganic water contaminants with biological and environmental issues.
- Know the sources of inorganic and organic contaminants.
- Differentiate between organic and inorganic substances when given a formula.

The US Safe Drinking Water Act defines the term "contaminant" as meaning any physical, chemical, biological, or radiological substance or matter in water. Therefore, the "contaminant" definition very broadly applies as being anything other than water molecules. Drinking water may reasonably be expected to contain at least small amounts of some contaminants. Some drinking water contaminants may be harmful if consumed at certain levels in drinking water while others may be harmless. The presence of contaminants does not necessarily indicate that the water poses a health risk.

Air Pollutants

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. Some of these compounds can become soluble in water. This could affect pH (or acidity) level of water surface water. Rain water with a pH below 5.6 is considered to be acid rain.

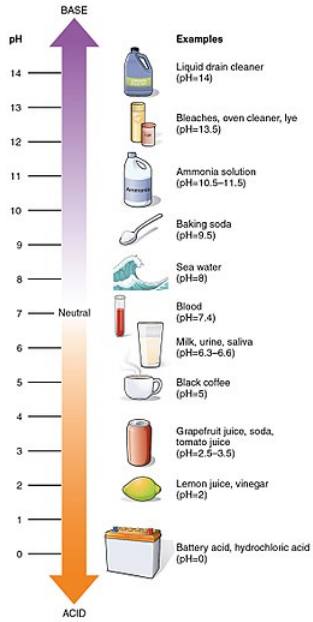


Figure **10.3.4.1**: pH scale. (Copyright; OpenStax College via Anatomy & Physiology, Connexions Web site. http://cnx.org/content/col11496/1.6/)

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 (H_2SO_4), nitric (HNO_3),** and **carbonic (H_2CO_3)**. This environmental problem affects living organisms and building materials. Acid solutions can corrode metals and make them soluble as well.

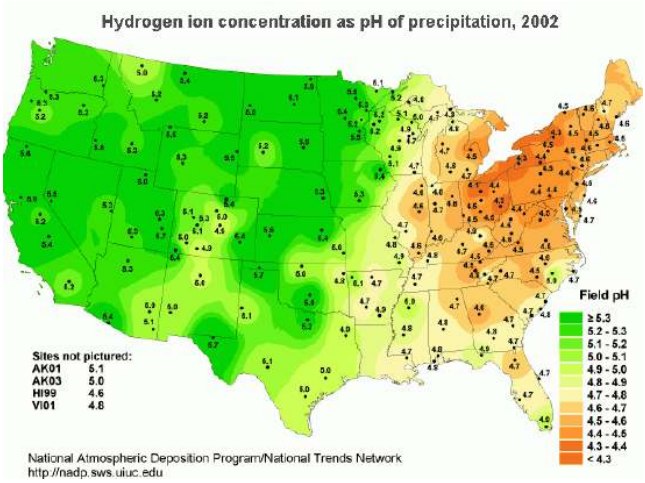


Figure **10.3.4.2**: pH of rainwater over the continental United States.

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. 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.

Acid rain from sulfuric acid

However, the majority of acid rain is accounted for by the presence of sulfuric acid ($\mathbf{H_2SO_4}$).

$$\mathrm{SO_2\,(g) + O_2\,(g) \longrightarrow SO_3\,(g)}$$

Sulfur dioxide reacts with water to form sulfuric acid

$$\mathrm{SO_3\,(g) + H_2O \longrightarrow H_2SO_4} \qquad (10.3.4.1)$$

Although sulfuric acid may be produced naturally in small quantities from biological decay and volcanic activity, it is produced almost entirely by human activity, especially the combustion of sulfur-containing fossil fuels in power plants.

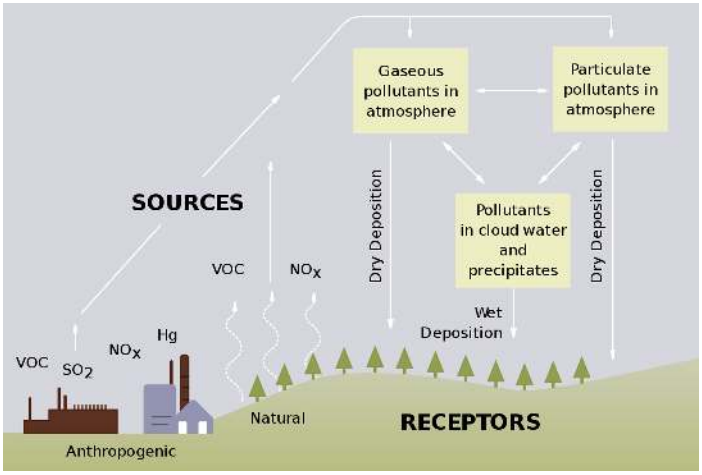


Figure **10.3.4.3**: Processes involved in acid deposition (note that only $\mathbf{SO_2}$ and $\mathbf{NOx}$ play a significant role in acid rain). (public domain; EPA)

Acid rain from nitric acid

Some of acid rain is accounted for by nitric acid ($\mathbf{HNO_3}$) that originates from natural processes, but especially from high-temperature air combustion, such as occurs in car engines and power plants, that produces large amounts of **NO** gas. This gas then forms nitric acid via several steps. First nitric oxide (**NO**) is formed during lightning storms by the reaction of nitrogen and oxygen

$$\mathbf{N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g)} \tag{10.3.4.2}$$

and **NO** is oxidized to nitrogen dioxide ($\mathbf{NO_2}$)

$$\mathbf{NO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow NO_2\,(g)} \tag{10.3.4.3}$$

$\mathbf{NO_2\,(g)}$ then reacts with water droplets to generate nitric acid ($\mathbf{HNO_3}$)

$$\mathbf{3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g)}$$

Table **10.3.4.2**: Source of Water contamination 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

Inorganic Contaminants

Solubility of these species can be determined by consulting a solubility table (e.g., Table 4.7.1). These chemicals might be naturally present in a water source. Industry and agriculture also use and dispose of these types of chemicals as well. In determining the source of any pollutant, it is helpful to know a region's geology and proximity to chemical consumers. In this section, we will focus on a few inorganic species that can affect drinking water quality.

Hard Water

When water is described as being hard, then this means it has a large concentration of minerals. The **ions** that contribute to this problem are **calcium** (Ca^{2+})**, magnesium** (Mg^{2+})**, carbonate** $(CO_3)^{2-}$, and **iron** (Fe^{2+}/Fe^{3+}). Hard water is not toxic, but can affect industrial processes. These ions will bond together to form insoluble salts that are called precipitates. Building up of these newly formed solids is called scale. Precipitates can collect in boilers, cooling towers, and any equipment that employs water. This buildup can affect how the equipment works by damaging it internally.

Video: Hard Water

Watch this video below to get an idea of what hard water is.



https://youtu.be/Ts6PNYk7-a0

1. What chemical species cause hard water?
2. How does hard water affect industry?
3. Hard water is known to contribute to the formation of kidney stones. How else can this type of water affect the body?

Soft Water

Soft water does not contain an excessive amount of alkaline minerals. Instead, **potassium** (K^+) and **sodium** (Na^+) ions are present. Soft water does not form scale but does produce excessive lathers with soap. Although industry and consumers prefer soft water, the sodium content can affect health if ingested at a high concentration.

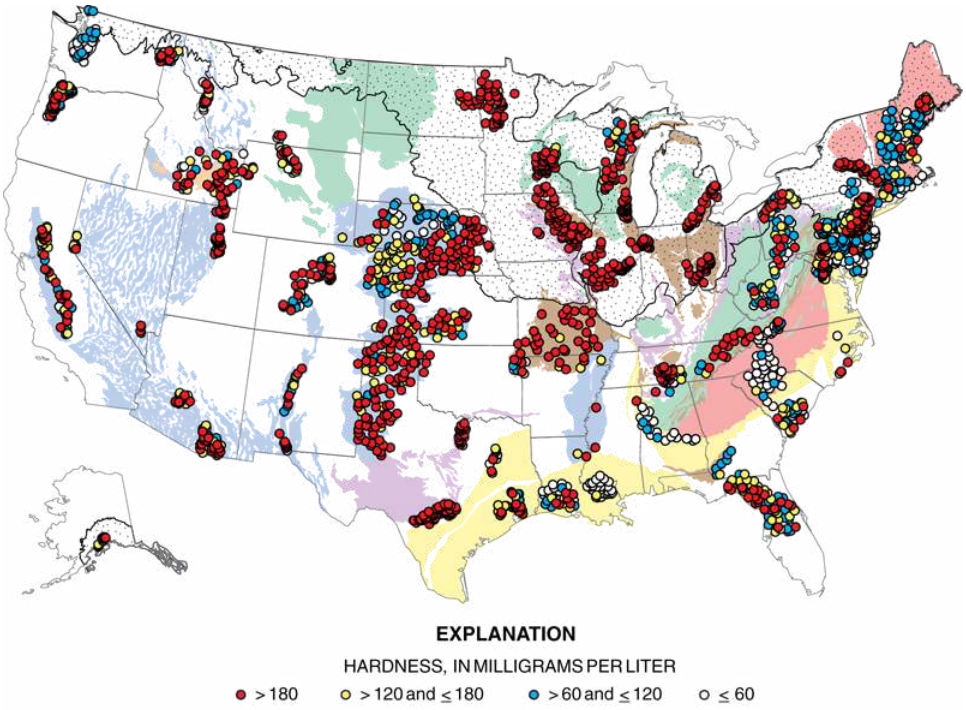


Figure **10.3.4.4**: Hardness of groundwater from domestic wells, a USGS study. A study from the National Water-Quality Assessment (NAWQA) Program assessed water-quality conditions for about 2,100 domestic wells across the United States. (Public Domain; USGS).

Eutrophication

When pollutants enter a water system they originate from either point or non-point sources. If a single identifiable source can be located, then the pollutant originated from a point source. In contrast, non point sources indirectly contaminant water, air, or soil. Examples of non-point sources would be run-off and acid rain. Obviously, non-point pollutants are more difficult to regulate.

In agriculture, nitrates $(NO_3)^-$ are used as fertilizers. Farmers can choose to use synthetic or natural (manure) nitrates. Regulating concentrations of these species could be difficult if all sources are not investigated and monitored. An excessive amount of these substances leads to eutrophication. Many nitrate $(NO_3)^-$ and phosphate $(PO_4)^{3-}$ containing compounds are soluble in water. Once dissolved, these substances can travel to lakes and ponds. Here, these chemicals activate plants and algae to grow. Overgrowth of plant-life in water can inhibit oxygen from entering the water. As a result, aquatic animals are more likely to die in this environment. In addition, decomposition of organic material (once living) will be slow and smelly.



Figure **10.3.4.5**: Algal bloom in village river. Taken in a small village in mountains near Chengdu, Sichuan, China. (CC BY-SA 3.0; River algae Sichuan - Trophic state index - Wikipedia)

Eutrophication can be halted in phosphate $(PO_4)^{3-}$ contamination is controlled. This involves limiting the use of some fertilizers and removing phosphates from detergents. Reducing nitrates can be a more challenging task. All compounds containing this polyatomic ion are extremely soluble. Moreover, controlling nitrate concentration from fecal material can be difficult.



Toxic Inorganic Species

Some inorganic compounds are quite soluble in water. If an aquatic system is acid, then solubility of these types of species can change. Lead and mercury based compounds are not as soluble as those in group IA of the periodic table. When the pH of water becomes acid, many of these once insoluble compounds now become dissolved and visually undetectable.

Lead (Action Level is 0.015 ppm)

Occupational exposure to lead is one of the most prevalent overexposures. Industries with high potential exposures include construction work, most smelter operations, radiator repair shops, and firing ranges. Other sources of lead based compounds include house paint (from before 1978), toys (older than 1976 or from abroad), pipes, faucets, jewelry, wet batteries (gasoline engine based), pottery, and Kohl/Kajol eyeliners.

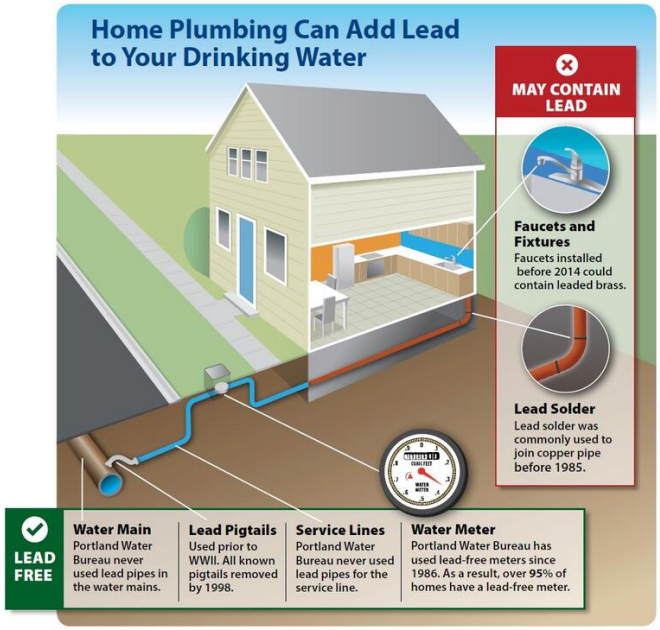


Figure **10.3.4.6**: Lead and drinking water. (Copyright; City of Portland)

Gasoline products may contain lead compounds to diminish knocking of a combustion engine. These additives increase the octane level of a fuel which enables the engine to burn more effectively. Unfortunately, releasing lead-based fumes can impair a person's nervous system. In addition, other disorders and diseases (kidney issues, gastrointestinal problems, growth delays, anemia, and learning difficulties) will become more prevalent in an area that has signification combustion of lead based fuels. Children will be more impacted by lead poisoning than adults. Often, the damage done to this group of people is irreversible. By the early 1970's, the Environmental Protection Agency (EPA) started focusing on phasing out leaded fuel products. By the mid 1980's, most US vehicles used only unleaded fuels. The EPA banned lead based fuel in 1996. Today, only the aviation industry and off-road vehicles are allowed to use leaded fuel in the United States.

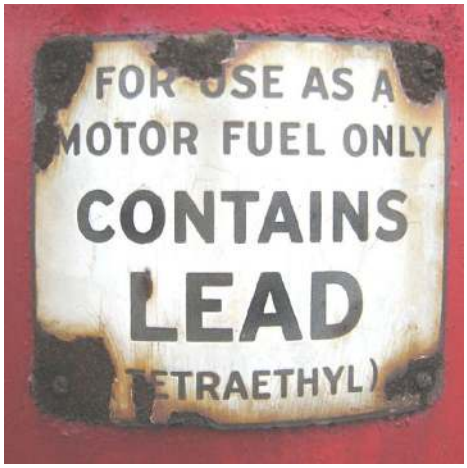


Figure **10.3.4.7**: ead warning on a gas pump at Keeler's Korner, Lynnwood, Washington. Keeler's Korner, a former grocery store and gas station (built 1927) listed on the National Register of Historic Places, listed 1982, NRHP listing #82004287. (CC-BY-SA 3.0; https://commons.wikimedia.org/wiki/User:Jmabel)

Arsenic (0.010 ppm or 10 ppb)

Common sources of exposure to higher-than-average levels of arsenic include near or in hazardous waste sites and areas with high levels naturally occurring in soil, rocks, and water.

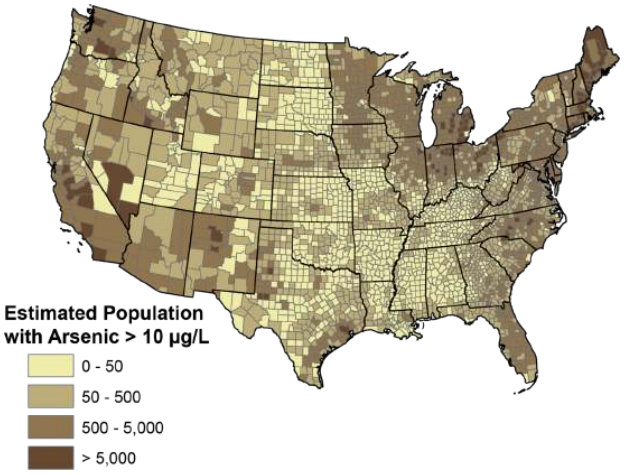


Figure **10.3.4.8**:This map shows estimates of how many private domestic well users in each county may be drinking water with levels of arsenic of possible concern for human health.(µg/L, micrograms per liter) (USGS; Arsenic and Drinking Water | U.S. Geological Survey (usgs.gov))

Arsenic compounds can be found in lead/copper smelting processes, lumber pressurizing (copper chromated arsenate compounds are no longer used in the United States) and pesticide applications (organic arsenic compounds are used to treat cotton fields and orchards). Exposure to high levels of arsenic can cause skin lesions, neurological problems, gastrointestinal/live illnesses, various cancers, and death.



Mercury (0.002 ppm)

Common sources of mercury exposure include mining, production, and transportation of mercury, as well as mining and refining of gold and silver ores. High mercury exposure results in permanent nervous system and kidney damage. Once inorganic mercury enters aquatic systems, it can transform into organic mercury or organometallic mercury. An example of one of these compounds is methyl mercury (CH_3Hg). This type of compound is quite toxic and has bioaccumulation effects.

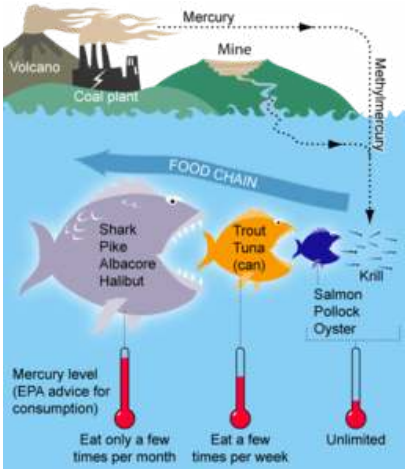


Figure 10.3.4.9: This figure shows some common sources of mercury, the conversion to toxic methylmercury and the outline of EPA consumption recommendations for certain types of fish based on mercury levels. (Copyright; Bretwood Higman, Ground Truth Trekking.via http://www.groundtruthtrekking.org/Graphics/Large/MercuryFoodChain-01.png)

Cadmium (0.005 ppm)

Cadmium is an extremely toxic metal that exists naturally in the Earth's crust as a common. Agricultural crops absorb cadmium compounds from the soil. The average person is exposed to cadmium through the consumption of plant based food, burning of cadmium based materials (air pollution), and drinking of tap water. Tobacco consumers receive additional cadmium when they smoke. Lastly, artists might use cadmium based pigments for dramatic colors in their paintings.



Figure 10.3.4.10: The Berkeley Pit, an open pit copper mine in Butte, Montana. (Copyright; User:Cybergrl23 via Wikipedica Commons)

At industrial workplaces, cadmium can be introduced to the atmosphere when any metal ore is being processed or smelted. Some forms of steel and batteries (Ni-Cd) contain cadmium mixtures. Several deaths from acute exposure have occurred among welders who have unsuspectingly welded on cadmium-containing alloys or with silver solders. This chemical substance is carcinogenic and causes a signature painful bone disease. Lastly, cadmium exposure can cause significant damage to kidneys.

Uranium (30 ppb)

Natural deposits of this element are found in the earth crust are sometimes associated with mountainous regions of the world. In the United States, uranium ores can be found in the western part of the country. If uranium becomes soluble, then it can leach or move to other locations contaminating water and soil nearby.

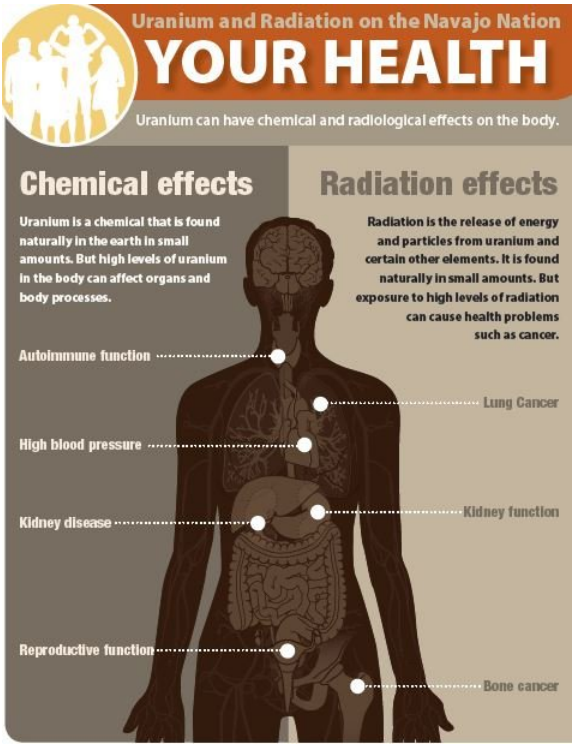


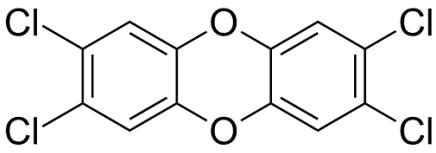
Figure 10.3.4.11: Your Health: Uranium and Radiation on the Navajo Nation. (epa.gov; Health Effects of Uranium | US EPA)

Enriched U-235 (2-5%) is used for fuel in all US commercial nuclear power plants. Waste products of fuel use are stored for long periods of time above ground at most nuclear reactor facilities. Fuel waste can be stored in a wet or dry environment. Either method requires isolation from humans and the environment since the waste will be radioactive for a long time. Enriched U-235 (90%) was fuel for the Little Boy atomic bomb which was dropped over Hiroshima in 1945. At the time, purification of this form of uranium was difficult and costly. This resulted in the production of only one uranium type atomic weapon.

Organic Chemical Concerns

Dioxin (3.0×10^{-8} ppm)

Dioxins are mainly byproducts of industrial practices. They are produced through a variety of incineration processes, including improper municipal waste incineration and burning of trash, and can be released into the air during natural processes, such as forest fires and volcanoes. Dioxins are also produced in the bleaching process used by the paper industry. These chemicals have been classified as Persistent Organic Polluters (POPS) because of their long residual life-times in the environment. These compounds are fat soluble and will accumulate in fatty tissues of living organisms which in turn affects the health of the food chain.



Dioxin based compounds harm hormonal and reproductive systems. In addition, immunity disorders and chloroacne can result if someone has been exposed to these types of chemicals. A famous case of intentional dioxin (TCDD) poisoning involved a former Ukrainian presidential candidate named Vicktor Yushchenko. In 2004, environmental toxicologists in Austria detected extremely high concentrations of dioxins in Yushchenko's blood. Also, medical experiments noted the change in his complexion before and after the poisoning. For more information regarding this incident, please click here.

When synthesizing Agent Orange (a herbicide used before and during the Vietnam War), chemists simultaneously and unintentionally produced dioxin. Exposure to this chemical derivative increased cancer rates to those exposed.



(PCB) Polychlorinated Biphenyls (5.0 x 10^{-4} ppm)

Once used as electrical insulators, the United States produced this family of compounds from the late 1930's through the 1970's. These compounds did not decompose, conduct electricity, and could withstand high temperature environments. For these reasons, PCBs were commonly incorporated into electrical transformers, fluorescent lights, capacitors and older household appliances (televisions and refrigerators).

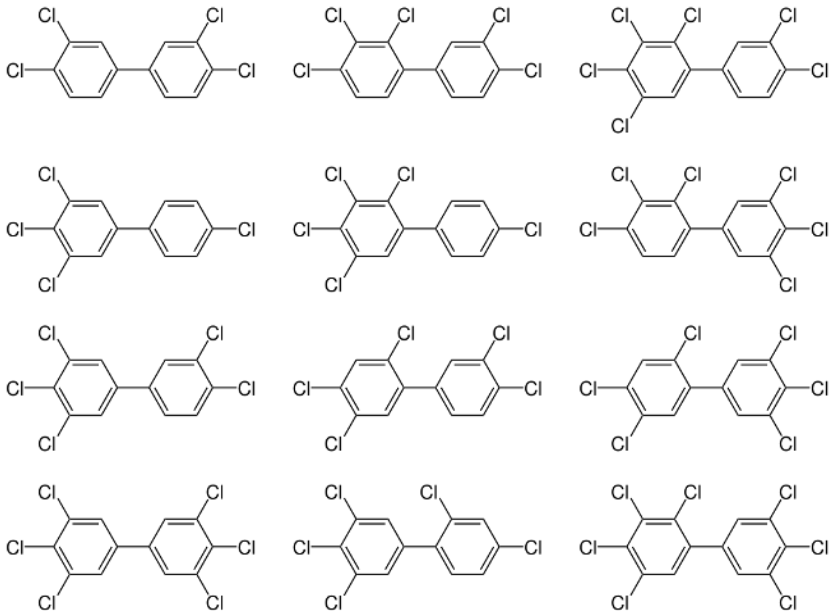


Figure **10.3.4.12**: Structures of dioxin-like PCBs.. (Copyright; User:Leyo via Own work based on: *M. Van den Berg et al. (2006). "The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds". Toxicological Sciences* ***93*** *(2): 223–241. DOI:10.1093/toxsci/kfl055. PMID 16829543.*)

These compounds are classified as human carcinogens. In certain concentrations, PCB exposure can manifest as chloracne. Chronic exposure to PCBs can cause liver and central nervous system damage. Lastly, PCBs can cause reproductive issues as well.

> file:///C:/Users/egordon/Downloads/c...disaster-5.pdf

References

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2. Lead Poisoning: Causes, Symptoms, and Diagnosis (healthline.com)
3. End Of Leaded Gasoline: World Has Stopped Using Toxic Additive : NPR
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5. Learn about Dioxin | US EPA

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10.3.5: Water Treatment

Water treatment is` a process of making water suitable for its application or returning its natural state. Thus, water treatment required before and after its application. The required treatment depends on the application. For example, treatment of greywater (from bath, dish and wash water) differs from the black water (from flush toilets). Composting toilet is not allowed in urban dwelling. Yet, composting toilets are used in a 30,000-square-foot office complex at the Institute of Asian Research, University of British Columbia.

Water treatment involves science, engineering, business, and art. The treatment may include mechanical, physical, biological, and chemical methods. As with any technology, science is the foundation, and engineering makes sure that the technology works as designed. The appearance and application of water is an art.

In terms of business, RGF Environmental, Water Energy Technologies, Aquasana Store, Vitech, Recalyx Industrial SDN BHD and PACE Chemicals ltd are some of many companies that offer various processes for water treatment. Millipore, a Fisher Scientific partner, offers many lines of products to produce *ultrapure water*, using a combination of active charcoal membranes, and reverse osmosis filter. Internet sites of these companies offer useful information regarding water.

An environmental scientist or consultant matches the service provider, modify if necessary, with the requirement.

- Natural Water includes some discussion on hard and soft water. Softening hard water for boiler, cooler, and domestic application is discussed therein. These treatments prepare water so that it is suitable for the applications.
- Water Biology deals with water and biology. Drinking water is part of making water suitable for living. Thus, this link gives some considerations to drinking water problems.
- There are many different industry types, and waters from various sources are usually treated before and after their applications. Pre-application treatment and wastewater treatment offer a special opportunity or challenge. Only a general consideration will be given to some industrial processes.
- General municipal and domestic wastewater treatment converts used water (waste) into environmentally acceptable water or even drinking water. Every urban centre requires such a facility.

General Wastewater Treatment

Water is a renewable resource. All water treatments involve the removal of solids, bacteria, algae, plants, inorganic compounds, and organic compounds. Removal of solids is usually done by filtration and sediment. Bacteria digestion is an important process to remove harmful *pollutants*. Converting used water into environmentally acceptable water or even drinking water is **wastewater treatment**

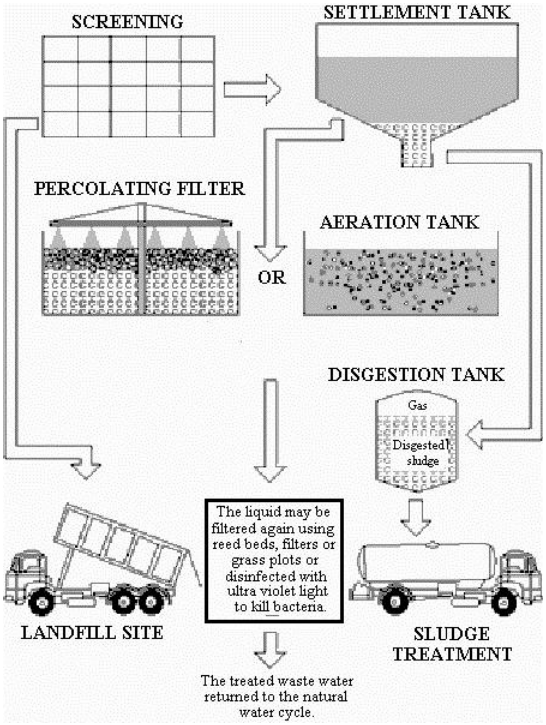
Water in the Great Lakes Region is an organization dealing with the water resources. Ontario Clean Water Agency (OCWA) is a provincial Crown corporation in business to provide environmentally responsible and cost-efficient water and wastewater services. It currently operates more than 400 facilities for 200 municipalities. This web site provides information on water and water treatment.

In April 1993, 403,000 people in Milwaukee were ill as a result of *cryptosporidium* contaimination of water due to spring run off. This outbreak caused the more stringent regulations to be implemented in the public dringking water system. The measures were aimed at removing cryptosporidium.

In May 2000, due to torrential downpour surface water got into shallow wells in a small town Walkerton, Ontario, Canada. On May 17, some residents complained of fever, bloody diarrhea and vomiting. This was know as the Walkerton *E. Coli* Outbreak. Nearly half of the population of the town fell ill, and several people died due to the E. Coli O157:H7 infection. A public inquiry recommended many measures to prevent similar outbreaks. These measures were aimed at eliminating E. Coli.

Sewage Treatment

As a general discussion, let us look at a typical process in sewage treatment. A flow diagram for a general sewage treatment plant from Water Education, Department of Computer Science, University of Exeter, U.K., is shown below:



Sewage is SCREENED to remove large solid chunks, which are disposed in LANDFILL SITE. It flows over to the SETTLEMENT TANK to let the fine particles to settle. The settlement is called the activated SLUDGE. The supernatant is then PERCOLATING FILTERED and/or AERATED. The water can be filtered again, and then disinfected (chlorinated in most cases). When there is no other complication, the water is returned to nature back to the ecological cycle.

The SLUDGE removed from the settlement is composed of living biological material. A portion of it may be returned to the AERATION TANK, but the raw SLUDGE is digested by both microorganism. Anaerobic (without oxygen) and aerobic (with air) bacteria digestions are used. At the digestion stage, carbon dioxide, ammonia, and methane gases are evolved. Volume of the digested sludge is reduced, and it is acceptable as a fertilizer supplement in farming.

Wastewater Treatment

Although the sewage water may be discharged back to the ecological system after AERATED DIGESTION and PERCOLATING FILTRATION, but in some cases, further treatment is required. Some general consideration of water treatment is given below.

A rather recent book, *Chemistry of Water Treatment* by S.D. Faust and O.M. Aly, 2nd Ed. (1998) [TD433 F38 1998], addresses the problem of quality natural and treated water.

The first three chapters discuss the criteria and standards for drinking water quality, organic compounds in waters, taste and order of water. Understandably, the standards change over the years. So are the standards of treated waters. Guidelines are available from government agencies such as Environment Canada which is equivalent to U.S. Public Health Service and the Environment Protection Agency (EPA). We have talked about drinking water in Water Biology.

Next seven chapters deal with the removal of the following:

- organics and inorganics by activated carbon
- particulate matter by coagulation
- particulate matter by filtration and sedimentation
- hardness and other scale-forming substances
- inorganic contaminants
- corrosive substances
- pathogenic (disease producing) bacteria, viruses, and protozoans (microorganisms).

There is a chapter dealing with **aeration**

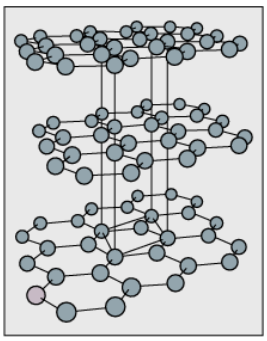
These items cover the chemistry, biology, and physics involved in the treatment of water. Some of these topics have been discussed in chemistry of water, physical properties of water, biology of water, and natural water. Introductions are going to be given to some selected topics below.

Treatment by Activated Carbon

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. Active research and production of activated charcoal was accelerated during the two world wars. The use of poison gas prompted the development of masks. They are still in use today.

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.



Charcoal consists of microcrystallites of graphite. The particles are so small in charcoal that they were considered amorphous. The crystal structure of graphite consists of layers of hexagonal networks, stacked on top of each other. Today, making activated carbon is a new and widely varied industry. Other molecules attach themselves to the porous surface and dangling carbons in these microcrystallites.

Carbon containing substances are charred at less than 900 K to produce carbon in the manufacture of **activated carbon**. However, the carbon is activated at 1200 K using oxidizing agent to selectively oxidize portions of the char to produce pores in the material. Because of the special process to produce used, these materials with high surface to mass ratio, they are called **activated carbon** rather than activated charcoal. Factors affecting the absorption are particle size, surface area, pore structure, acidity (pH), temperature, and the nature of the material to be absorbed. Usually, adsorption (absorption) equilibria and rate of adsorption must be considered for effective applications.

Coagulation, Flucculation and Sedimentation

Natural and wastewater containing small particulates. They are suspended in water forming a **colloid**. These particles carry the same charges, and repulsion prevents them from combining into larger particulates to settle. Thus, some chemical and physical techniques are applied to help them settle. The phenomenon is known as **coagulation**. A well known method is the addition of electrolyte. Charged particulates combine with ions neutralizing the charges. The neutral particulates combine to form larger particles, and finally settle down.

Another method is to use high-molecular-weight material to attract or trap the particulates and settle down together. Such a process is called **flocculation**. Starch and multiply charged ions are often used.

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:

$$Al2(SO4)3.12\ H2O, \rightarrow Al(aq)3+ + 3\ SO4(aq)2- + 12\ H2O$$
$$SO4(aq)2- + H2O \rightarrow HSO4(aq)- + OH- \text{ (causing pH change)}$$
$$Ca(OH)2 \rightarrow Ca(aq)2+ + 2\ OH- \text{ (causing pH change)}$$

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 let the water sit around to let the floculated or coagulated particles to settle out. It works best with relatively dense particles (e.g. silt and minerals), while flotation works better for lighter particles (e.g. algae, color). A settling tank should be big enough so that it takes a long time (ideally 4 hours +) to get through. Inlets and outlets are designed so the water moves slowly in the tank. Long and narrow channels are installed to let the water to snake its way through the tank. The settled particles, sludge, must occasionally be removed from the tanks. The water is next ready to be filtered. Sedimentation is used in pre-treatment and wastewater treatment.

Filtration

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.

The process of removing the clogged portion of the filter bed by reversing the flow through the bed and washing out the solid is called **back washing**. During this process, the solid must be removed out of the system, but otherwise the filters must be either replaced or taken out of service to be cleaned.

Aqua-Rain manufacture water filters as shown here. This unit consists of four filters. Regarding the filtering system, its technical info gave the following statement.



> *At the heart of the AquaRain™ Water Filtration System are Marathonr State-of-the-art ceramic elements utilizing a long-proven filtration process that is over 100 years old which will safely remove dangerous waterborne pathogens such as cysts (Cryptospordium, Giardia lamblia) and bacteria (E. coli, Samonelli typhus, etc...). These innovative Marathonr ceramic elements are also filled with a high grade silvered granulated activated carbon (GAC). The GAC reduces pesticides, chemicals, chlorine, tastes & odors, while leaving the naturally occurring minerals found in the water unaffected.*

The units are designed for emergency and perhaps undeveloped countries.

AquaSelect of Mississauga has a pitcher water filter system, and *its cartridge contains hundreds of high efficiency activated carbon and ion exchange beads*, its web site claims. Brita filters is very popular.

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.

A gas or substance dissolved in water may further react with water. Such a reaction is called **hydration**. Ionic substance dissolve due to hydration, for example:

$$\mathrm{HCl(g) + \mathit{x}\,H_2O \rightleftharpoons H(H_2O)_\mathit{x}^{+} + Cl(aq)^{-}} \tag{10.3.5.1}$$

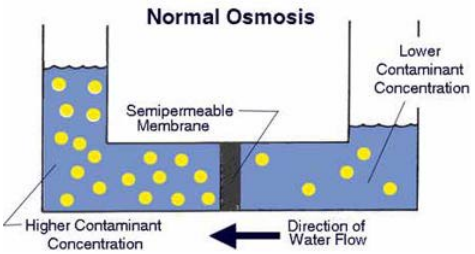
$$\mathrm{H_2S \rightleftharpoons H^{+}(aq) + HS^{-}(aq)} \tag{10.3.5.2}$$

These reactions are reversible, and aeration may also causes dehydration resulting in releasing the gas from water. Henry's law is applicable to this type of equilibrium for consideration. Methods of aeration are

- Diffused aeration - Air bubbles through water.

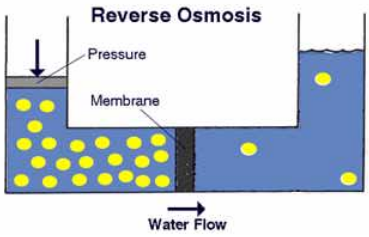
- Spray aeration - Water is sprayed through air.
- Multiple-tray aeration - Water flows through several trays to mix with air.
- Cascade aeration - Water flows downwards over many steps in the form of thin water falls.
- Air stripping - A combination of multiple tray and cascade technique plus random packed blocks causing water to mix thoroughly with air.

Reverse Osmosis Water Filter System



In the following discussion, a dilute solution and a concentrated solution are considered. The dilute solution can be a clean water whereas the concentrated solution contains undesirable solute (electrolyte or others).

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. Pig bladders are natural semipermeable membranes. As the water molecules migrate through the semipermeable membrane, water level in the solution will increase until the (osmotic) pressure prevents a net migration of water molecules in one direction. A pressure equivalent to the height difference is called the osmotic pressure. The illustration given on the right is from the PurePro, one of the many companies that manufacture reverse osmosis water filter devices. Millipore also use this technique.



By applying pressure in the higher concentration solution, water molecules migrate from a high concentration solution to a low concentration solution. This method is called **reverse osmosis water filter system**. The concept of reverse osmosis is illustrated in the diagram here from PurePro.

In this technique, the membrane must be able to tolerate the high pressure, and prevent solute molecules to pass through. Regarding membranes, PurePro made the following statement:

> *Semipermeable membranes have come a long way from the natural pig bladders used in the earlier osmosis experiments. Before the 1960's, these membranes were too inefficient, expensive, and unreliable for practical applications outside the laboratory. Modern advances in synthetic materials have generally solved these problems, allowing membranes to become highly efficient at rejecting contaminants, and making them tough enough to withstand the greater pressures necessary for efficient operation.*

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. Free Drinking Water also uses reverse osmosis filter system for domestic applications.

Industrial Wastewater Treatment

The Environment Canada's (Atlantic Region) Waste Management and Remediation Section contains links to detailed information on the programs and activities relating to Petroleum and Allied Petroleum Storage Tank Systems, Ocean Disposal, Contaminated Sites, and Hazardous Waste Disposal Advice for the provinces of Newfoundland and Labrador, Nova Scotia, New Brunswick and Prince Edward Island. It also contains links to sites within and outside of Environment Canada with related information.

Contributors and Attributions

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10.3.6: PBBs

Polybrominated Biphenyls (PBBs)

The Michigan Chemical Company in St. Louis, Michigan produced two chemicals, ok they produced more than two but this story involves only two. One day in early 1973, there was a shortage of preprinted paper bag containers which led to misidentification of materials. Ten to twenty 50-pound bags of polybrominated biphenyl, specifically BP-6, accidentally being sent to Michigan Farm Bureau Services in place of NutriMaster, a magnesium oxide cattle feed supplement. Of course these two chemical compounds look similar enough that the mix up was not discovered. Well it was not discovered until April 1974 and by that time PBB had entered the food chain through milk, other dairy products, beef products, and contaminated swine, sheep, chickens and eggs.

So what are PBBs?

They are a class of biphenyl compounds with one to ten hydrogen atoms replaced by bromine. There are 209 possible compounds, referred to as PBB congeners, which differ in the number and position of the bromine atoms on the two phenyl rings.

PBBs with three or more bromines are solids with low volatility and the volatility decreases further as more hydrogens are replaced. PBBs are very stable. They are insoluble in water but readily soluble in fat.

So what do these properties of PBBs mean for organisms that consume them?

Because PBBs are fat soluble, when PBBs are ingested, such as in the contaminated feed, the organism assimilates the PBBs in fat cells in the body. They are very stable and will remain in the fat cells.

What happens if an organism consumes another meal containing PBB contaminates?

Termed bioaccumulation, the organism now has two doses of PBB in its fat cells.

Let's say some mice ate contaminated feed. What would you predict about the barn cat that fed on the mice?

Termed Ecological magnification, organisms higher in the food chain will assimilate larger quantities of fat soluble toxins.

What concerns would you have for new mothers and their young? What would you recommend?

Breast feeding passes fat cells in the mother's milk along to the baby. Since these toxins are accumulated in fat cells, the toxins would also be passed along.

So what was the fallout from Michigan's accidental chemical switch?

Failure to identify the mix up early on resulted in widespread contamination of farm animals requiring the destruction of thousands of contaminated livestock cattle, hogs and sheep, millions of poultry. Approximately 865 tons of animal feed, 17,790 pounds of cheese, 2630 pounds of butter, 34000 pounds of dry milk and nearly 5 million eggs were destroyed. A large number of health problems have been reported by people consuming contaminated food. Tests on people in the area, livestock and livestock products, soil and water have been conducted on a regular basis to track presence and concentrations of PBBs. It has been found that this compound is persistent in fat tissue and soils, especially those high in clay. (Di Carlo)

From ChemPRIME: 8.8: Aromatic Hydrocarbons

References:

EFSA Panel on Contaminants in the Food Chain (CONTAM); Scientific Opinion on Polybrominated Biphenyls (PBBs) in Food. EFSA Journal 2010; 8(10):1789. [151 pp.]. doi:10.2903/j.efsa.2010.1789. Available online: www.efsa.europa.eu/efsajournal

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10.4: Solids

Learning Objective

- Describe the general properties of a solid.
- Describe the six different types of solids.

A solid is like a liquid in that particles are in contact with one another. Solids are unlike liquids in that the intermolecular forces are strong enough to hold the particles in place. At low enough temperatures, all substances are solids (helium is the lone exception), but the temperature at which the solid state becomes the stable phase varies widely among substances, from 20 K (−253°C) for hydrogen to over 3,900 K (3,600°C) for carbon.

The solid phase has several characteristics. First, solids maintain their shape. They do not fill their entire containers like gases do, and they do not adopt the shape of their containers like liquids do. They cannot be easily compressed like gases can, and they have relatively high densities.

Solids may also demonstrate a variety of properties. For example, many metals can be beaten into thin sheets or drawn into wires, while compounds such as NaCl will shatter if they are struck. Some metals, such as sodium and potassium, are rather soft, while others, such as diamond, are very hard and can easily scratch other substances. Appearances differ as well: most metals are shiny and silvery, but sulfur (a nonmetal) is yellow, and ionic compounds can take on a rainbow of colors. Solid metals conduct electricity and heat, while ionic solids do not. Many solids are opaque, but some are transparent. Some dissolve in water, but some do not. Figure **10.4.1**, shows two solids that exemplify the similar and dissimilar properties of solids.



Figure **10.4.1**: Properties of Solids. (a) Sodium metal is silvery, soft, opaque, and conducts electricity and heat well. (b) NaCl is transparent, hard, colorless, and does not conduct electricity or heat well in the solid state. These two substances illustrate the range of properties that solids can have. Source: Photo on left courtesy of Images of Elements, http://images-of-elements.com/sodium.php. Photo on right courtesy of Choba Poncho, commons.wikimedia.org/wiki/File:Sodiumchloride_crystal_01.jpg.

Solids can have a wide variety of physical properties. We will review the different types of solids and the bonding that gives them their properties.

First, we must distinguish between two general types of solids. An **amorphous solid** is a solid with no long-term structure or repetition. Examples include glass and many plastics, both of which are composed of long chains of molecules with no order from one molecule to the next. A **crystalline solid** is a solid that has a regular, repeating three-dimensional structure. A crystal of NaCl (Figure **10.4.1**) is one example: at the atomic level, NaCl is composed of a regular three-dimensional array of Na^+ ions and Cl^- ions.

There is only one type of amorphous solid. However, there are several different types of crystalline solids, depending on the identity of the units that compose the crystal.

An **ionic solid** is a crystalline solid composed of ions (even if the ions are polyatomic). NaCl is an example of an ionic solid (Figure **10.4.2** - An Ionic Solid). The Na^+ ions and Cl^- ions alternate in three dimensions, repeating a pattern that goes on throughout the sample. The ions are held together by the attraction of opposite charges—a very strong force. Hence most ionic

solids have relatively high melting points; for example, the melting point of NaCl is 801°C. Ionic solids are typically very brittle. To break them, the very strong ionic attractions need to be broken; a displacement of only about 1×10^{-10} m will move ions next to ions of the same charge, which results in repulsion. Ionic solids do not conduct electricity in their solid state; however, in the liquid state and when dissolved in some solvent, they do conduct electricity. This fact originally promoted the idea that some substances exist as ionic particles.

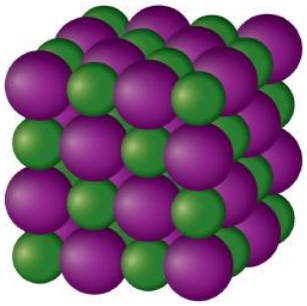


Figure 10.4.2: An Ionic Solid. NaCl is a solid composed of a three-dimensional array of alternating Na^+ ions (green) and Cl^- ions (purple) held together by the attraction of opposite charges.

A **molecular solid** is a crystalline solid whose components are covalently bonded molecules. Many molecular substances, especially when carefully solidified from the liquid state, form solids where the molecules line up with a regular fashion similar to an ionic crystal, but they are composed of molecules instead of ions. Because the intermolecular forces between molecules are typically less strong than in ionic solids, molecular solids typically melt at lower temperatures and are softer than ionic solids. Ice is an example of a molecular solid. In the solid state, the molecules line up in a regular pattern (Figure 10.4.3). Some very large molecules, such as biological molecules, will form crystals only if they are very carefully solidified from the liquid state or, more often, from a dissolved state; otherwise, they will form amorphous solids.

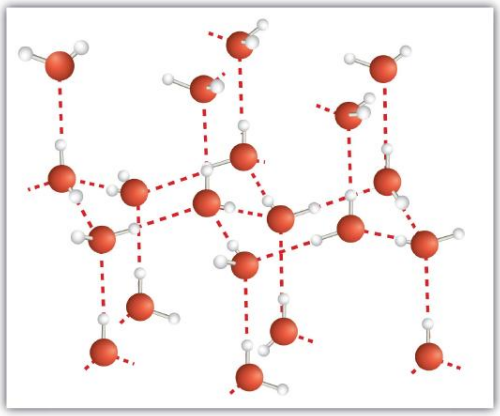


Figure 10.4.3: Molecular Solids. Water molecules line up in a regular pattern to form molecular solids. The dotted lines show how the polar O–H covalent bonds in one molecule engage in hydrogen bonding with other molecules. The O atoms are red, and the H atoms are white.

Some solids are composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion. Such solids are called **covalent network solids**. Each piece of the substance is essentially one huge molecule, as the covalent bonding in the crystal extends throughout the entire crystal. The two most commonly known covalent network solids are carbon in its diamond form and silicon dioxide (SiO_2). Figure 10.4.4 - Covalent Network Solids, shows the bonding in a covalent network solid. Generally, covalent network solids are poor conductors of electricity, although their ability to conduct heat is variable: diamond is one of the most thermally conductive substances known, while SiO_2 is about 100 times less thermally conductive. Most covalent network solids are very hard, as exemplified by diamond, which is the hardest known substance. Covalent network solids have high melting points by virtue of their network of covalent bonds, all of which would have to be broken for them to transform into a liquid. Indeed, covalent network solids are among the highest-melting substances known: the

melting point of diamond is over 3,500°C, while the melting point of SiO_2 is around 1,650°C. These characteristics are explained by the network of covalent bonds throughout the sample.

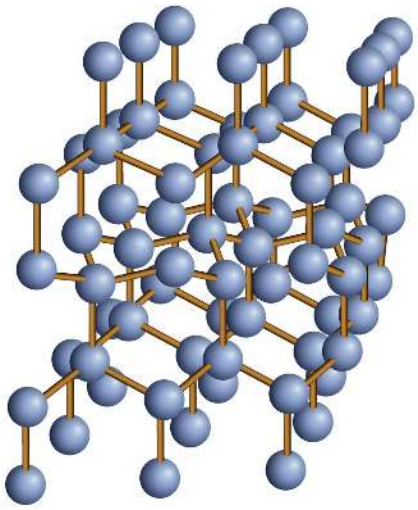


Figure **10.4.4**: Covalent Network Solids. Diamond is a covalent network solid, with each C atom making four covalent bonds to four other C atoms. A diamond is essentially one huge molecule.

A **metallic solid** is a solid with the characteristic properties of a metal: shiny and silvery in color and a good conductor of heat and electricity. A metallic solid can also be hammered into sheets and pulled into wires. A metallic solid exhibits metallic bonding, a type of intermolecular interaction caused by the sharing of the *s* valence electrons by all atoms in the sample. It is the sharing of these valence electrons that explains the ability of metals to conduct electricity and heat well. It is also relatively easy for metals to lose these valence electrons, which explains why metallic elements usually form cations when they make compounds.

✔ Example 10.4.1

Predict the type of crystal exhibited by each solid.

a. MgO
b. Ag
c. CO_2

Solution

a. A combination of a metal and a nonmetal makes an ionic compound, so MgO would exist as ionic crystals in the solid state.
b. Silver is a metal, so it would exist as a metallic solid in the solid state.
c. CO_2 is a covalently bonded molecular compound. In the solid state, it would form molecular crystals. (You can actually see the crystals in dry ice with the naked eye.)

? Exercise 10.4.1

Predict the type of crystal exhibited by each solid.

a. I_2
b. $Ca(NO_3)_2$

Answers

a. molecular crystals
b. ionic crystals

Food and Drink Application: The Rocks We Eat

The foods and beverages we eat and drink all have different phases: solid, liquid, and gas. (How do we ingest gases? Carbonated beverages have gas, which sometimes cause a person to belch.) However, among the solids we eat, three in particular are, or are produced from, rocks. Yes, rocks!

The first one is NaCl, or common salt. Salt is the only solid that we ingest that is actually mined as a rock (hence the term *rock salt*; it really is a rock). Salt provides both Na^+ ions and Cl^- ions, both of which are necessary for good health. Salt preserves food, a function that was much more important before the days of modern food preparation and storage. The fact that saltiness is one of the major tastes the tongue can detect suggests a strong evolutionary link between ingesting salt and survival. There is some concern today that there is too much salt in the diet; it is estimated that the average person consumes at least three times as much salt daily as is necessary for proper bodily function.

The other two rocks we eat are related: sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). However, we do not mine these substances directly from the ground; we mine trona, whose chemical formula is $Na_3H(CO_3)_2$. This substance is dissolved in water and treated with CO_2 gas to make either Na_2CO_3 or $NaHCO_3$. Another process, called the Solvay process, is also used to make Na_2CO_3. In the Solvay process, NH_3 and CO_2 are added to solutions of NaCl to make $NaHCO_3$ and NH_4Cl; the $NaHCO_3$ precipitates and is heated to produce Na_2CO_3. Either way, we get these two products from the ground (i.e., rocks).

$NaHCO_3$ is also known as baking soda, which is used in many baked goods. Na_2CO_3 is used in foods to regulate the acid balance. It is also used in laundry (where it is called washing soda) to interact with other ions in water that tend to reduce detergent efficiency.



Figure **10.4.5**: Salt Mining © Thinkstock. Salt mining can be at the surface or below ground. Here salt is mined from surface deposits. Part of the processing facility can be seen in the background.

Summary

- Solids can be divided into amorphous solids and crystalline solids.
- Crystalline solids can be ionic, molecular, covalent network, or metallic.

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10.4.1: Fats and Lipids in Bioamplification

One important consequence of the hydrophobic character of lipids is the concentration of nonpolar substances along ecological food chains, a process known as **bioamplification**. As an example, consider organisms in an aqueous environment such as a river or lake. Any substance which is more soluble in living tissues than in the surrounding water will tend to concentrate in even the simplest plants and animals. These plants and animals are often the food supply for more complex life forms—a food supply which contains a greater concentration of the substance in question. As we proceed up the food chain to larger predatory animals, the concentrations of some substances can be increased by factors of 10 000 or more.

What kinds of substances are likely to undergo bioamplification? Clearly those which are more soluble in living systems. Since the surroundings are dilute aqueous solutions while organisms contain both aqueous and lipid phases, nonpolar substances which dissolve in lipids are most likely to be concentrated. This is a problem with DDT, polychlorinated biphenyls (PCB's), and other long-lived synthetic organic compounds. It also applies to metal ions which can combine with organic groups to form uncharged molecules. A good example of such an organometallic compound involves mercury. Certain aquatic microorganisms can convert relatively inert mercury metal into chloromethylmercury(II) (commonly known as methylmercuric chloride):

$$\mathrm{Hg} \xrightarrow[\text{microorganisms}]{\text{aquatic}} \mathrm{CH_3{-}Hg{-}Cl}$$

Since the charge of Hg^{2+} is neutralized by Cl_3^- and Cl^-, this organometallic compound is quite soluble in lipid tissues. Concentration of mercury along aquatic food chains has led to several episodes where hundreds of Japanese people whose diet consisted mainly of fish became ill and many died. It also accounts for the relatively high level of mercury observed in some species of fish taken from the Great Lakes of the United States and Canada.

Humans and other organisms do have mechanisms for eliminating toxic and otherwise undesirable organic substances. A wide variety of enzymes in the human liver can convert hydrophobic molecules to more polar forms which are less soluble in lipid tissues and more readily excreted. However, there is often a problem with synthetic substances which have been synthesized by chemists and whose structures are quite different from any the liver enzymes are equipped to handle. As in the case of the ABS detergents, the reactions which decompose such substances may be relatively slow. If they are not converted into structures which can be eliminated easily, even small quantities may remain in the body for long periods, sometimes causing chronic illness. It is for this reason that toxic effects of synthetic organic or organometallic chemicals should be thoroughly tested before large quantities are released to the environment.

From ChemPRIME:20.3: Fats and Lipids

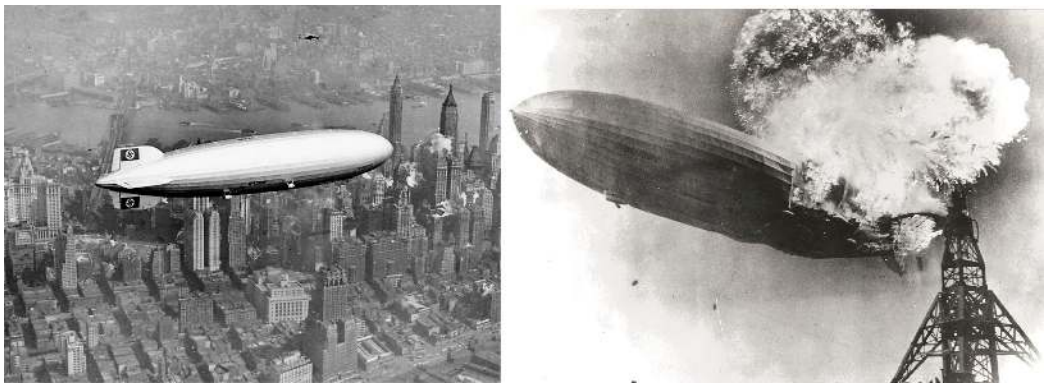
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10.5: Prelude to Gases

Perhaps one of the most spectacular chemical reactions involving a gas occurred on May 6, 1937, when the German airship *Hindenburg* exploded on approach to the Naval Air Station in Lakehurst, New Jersey. The actual cause of the explosion is still unknown, but the entire volume of hydrogen gas used to float the airship, about 200,000 m^3, burned in less than one minute. Thirty-six people, including one on the ground, were killed. Hydrogen is the lightest known gas. Any balloon filled with hydrogen gas will float in air if its mass is not too great. This makes hydrogen an obvious choice for flying machines based on balloons—airships, dirigibles, and blimps.



The German airship Hindenburg (left) was one of the largest airships ever built. However, it was filled with hydrogen gas and exploded in Lakehurst, New Jersey, at the end of a transatlantic voyage in May 1937 (right).

However, hydrogen also has one obvious drawback—it burns in air according to the well-known chemical equation:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

So although hydrogen is an obvious choice, it is also a dangerous choice. Helium gas is also lighter than air and has 92% of the lifting power of hydrogen. Why, then, was helium not used in the *Hindenburg*? In the 1930s, helium was much more expensive. In addition, the best source of helium at the time was the United States, which banned helium exports to pre–World War II Germany. Today all airships use helium, a legacy of the *Hindenburg* disaster.

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10.5.1: Kinetic Theory of Gases

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. The kinetic theory of gases is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic—that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 10.5.1.1 shows a representation of how we mentally picture the gas phase.

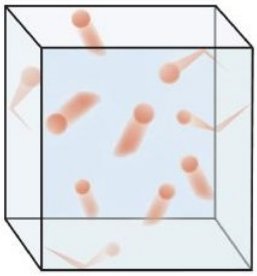


Figure 10.5.1.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements, and the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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10.6: Prelude to Solutions

More than 70% of the earth's surface is covered by a very important solution—seawater. It is likely that without seawater, no life would exist on Earth.

At its simplest, seawater is mostly H_2O. However, about 3.5% of seawater is dissolved solids—mostly NaCl—but other ions as well. Table **10.6.1** lists the percentage by mass of the various ions in seawater. Because it is highly likely that life on Earth originated in the oceans, it should not be surprising that many bodily fluids resemble seawater, especially blood. Table **10.6.1** also lists the percentage by mass of ions in a typical sample of blood.

Table **10.6.1**: Percentage by Mass of Ions in Seawater and Blood

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

Most ions are more abundant in seawater than they are in blood, with some notable exceptions. There is far more hydrogen carbonate ion (HCO_3^-) in blood than in seawater; indeed, it is the third most common ion in blood. This difference is significant because the HCO_3^- ion and some related species [CO_3^{2-}, $CO_2(aq)$] have an important role in controlling the acid-base properties of blood. Although there is a negligible amount of the two hydrogen phosphate ions (HPO_4^{2-} and $H_2PO_4^-$) in seawater, there is a small amount in blood, where these ions affect acid-base properties. Another notable difference is that blood has a negligible amount of the sulfate ion (SO_4^{2-}), but this ion is present in seawater. Gold is present in seawater—but only a tiny amount. A current estimate of the amount of gold is about 1 part per every 1×10^{13} parts of seawater, which makes the extraction of gold from seawater unfeasible. However, it does mean that there are about 1.4×10^{14} g of gold in the world's oceans!



Figure **10.6.1**: Gold in the Ocean. There are approximately 1.4×10^{14} g of gold in the oceans, but extracting it effectively is beyond current technologies. (CC SA-BY; Evgeni Dinev, Flickr.)

A solution is a *homogeneous mixture*: a mixture of two or more substances that are so intimately mixed that the mixture behaves in many ways like a single substance. Many chemical reactions occur when the reactants are dissolved in solution. In this chapter, we will introduce concepts that are applicable to solutions and the chemical reactions that occur in them.

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10.6.1: Definitions

Learning Objective

- Learn some terminology involving solutions.
- Recognize which terminology is qualitative and which terminology is quantitative.
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. "Major" and "minor" indicate which component has the greater or lesser presence by mass or moles, respectively. Sometimes this becomes confusing, especially when considering substances with very different molar masses. We will confine the discussion here to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water; soda water is a solution of gaseous CO_2 in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent.

Example 10.6.1.1: Sugar 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 10.6.1.1

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

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called **concentration**. Various words are used to describe the relative amounts of solute. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table **10.6.1.1** lists the solubilities of some simple ionic compounds. These solubilities vary widely: NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table **10.6.1.1**: Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated but rather concentrated. Ideally, we need more precise ways of specifying the amount of solute in a solution. We will introduce such ways in Section 11.3.

In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.

It should be obvious that some solutes dissolve in certain solvents but not others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not water. 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 Chapter 10). 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. This concept leads to the general rule that "like dissolves like" for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

✔ Example 10.6.1.2: 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 10.6.1.2

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

Answer

H_2O because both experience hydrogen bonding

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration is the expression of the amount of solute in a given amount of solvent and can be described by several qualitative terms.
- Solubility is a specific amount of solute that can dissolve in a given amount of solvent.

- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

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10.7: Introduction to energy

It takes energy to launch a spaceship into space. If it takes 1 energy unit to warm 0.25 g of water by 1°C, then it takes over 15,100 energy units to put that 0.25 g of water into earth orbit. The most powerful engines designed to lift rockets into space were part of the Saturn V rocket, that was built by the National Aeronautics and Space Administration (NASA). The rocket had three stages, with the first stage having the capability to launch about 3.5 million kg of mass. About 2.3 million kg was the actual fuel for the first stage; rockets in space have the unpleasant task of having to take their own chemicals with them to provide thrust.



Figure 10.7.1: Saturn V SA-513 lifts off to boost the Skylab Orbital Workshop into Earth orbit. It takes a lot of energy to launch a rocket into space. The Saturn V rocket used five of the most powerful engines ever built to take its initial step into orbit. (Public Domain; NASA)

Having to carry its own fuel puts a lot of mass burden on an engine in space. This is why NASA is developing other types of engines to minimize fuel mass. An ion thruster uses xenon atoms that have had at least one electron removed from their atoms. The resulting ions can be accelerated by electric fields, causing a thrust. Because xenon atoms are very large for atoms, the thrusting efficiency is high even though the actual thrust is low. Because of this, ion engines are useful only in space.

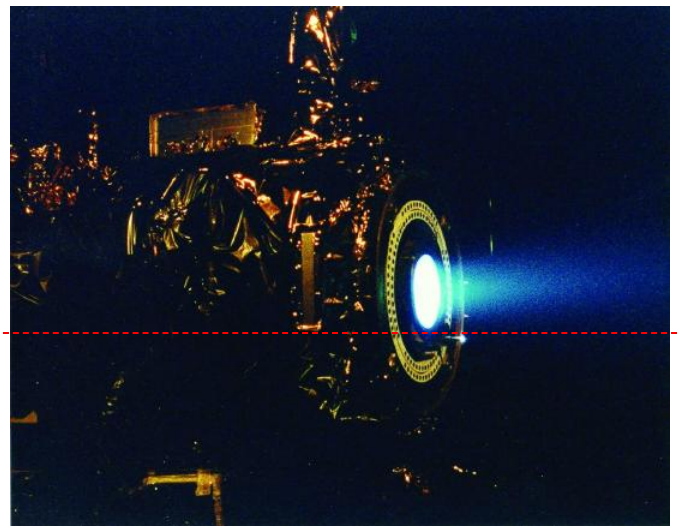


Figure 10.7.2: An Ion Thruster. Ion drives have low thrust, but high efficiency. They have already been used on several space missions, including NASA's Deep Space 1 spacecraft and Japan's Hayabusa asteroid sampling probe. Source: Photo courtesy of NASA, commons.wikimedia.org/wiki/File:Ion_Engine_Test_Firing_-_GPN-2000-000482.jpg.

Energy is a very important quantity in science and the world around us. Although most of our energy ultimately comes from the sun, much of the energy we use on a daily basis is rooted in chemical reactions. The gasoline in your car, the electricity in your

house, the food in your diet—all provide substances for chemical reactions to provide energy (gasoline, food) or are produced from chemical reactions (electricity, about 50% of which is generated by burning coal). As such, it is only natural that the study of chemistry involves energy.

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10.7.1: Energy and Chemical Bonds

Learning Objectives

- Define energy and distinguish the different types of energy, potential and kinetic.

Chemical changes and their accompanying changes in *energy* are important parts of our everyday world (Figure **10.7.1.1**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



Figure **10.7.1.1**: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, often referred to as *stored energy*, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure **10.7.1.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **10.7.1.2**: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. **Heat** is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

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10.7.2: Exothermic and Endothermic Reactions

Learning Objectives

- Use bond dissociation energies to calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. Endothermic reactions *require* energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases (ΔH is positive). As discussed in the previous section, heat is released (considered a product) in an exothermic reaction, and the enthalpy of the system decreases (ΔH is negative).

In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases (gets cold). A chemical reaction is exothermic if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, the temperature of the surroundings increases. See Figure 10.7.2.1.

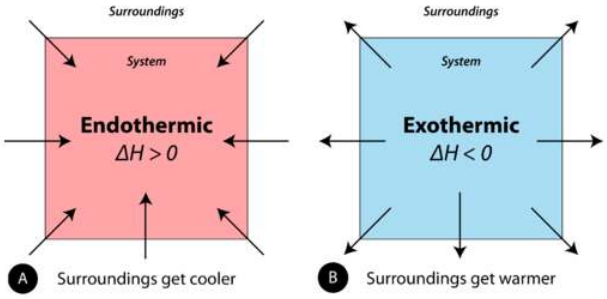


Figure 10.7.2.1: (A) Endothermic reaction. (B) Exothermic reaction.

Endothermic Reaction: When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. Because the heat is absorbed by the system, the 177.8 kJ is written as a *reactant*. The ΔH is *positive* for an endothermic reaction.

Heat is a reactant

$$CaCO_3\,(s) + 177.8\ \text{kJ} \rightarrow CaO\,(s) + CO_2\,(g)$$

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \quad \Delta H = +177.8\ \text{kJ} \tag{10.7.2.1}$$

Exothermic Reaction: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the product side of the reaction. Another way is to write the ΔH information with a *negative* sign, $-890.4\ \text{kJ}$.

Heat is a product

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + 890.4\ \text{kJ}$$

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \quad \Delta H = -890.4\ \text{kJ} \tag{10.7.2.2}$$

Example 10.7.2.1

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.

b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

? Exercise 10.7.2.1

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\ (g) + 130\ kcal$

b. $2C(s) + H_2(g) + 5.3\ kcal \rightarrow C_2H_2(g)$

Answer

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in Figure **10.7.2.2**. In endothermic reactions, the reactants have higher bond energy (*stronger bonds*) than the products. Strong bonds have lower potential energy than weak bonds. Hence, the energy of the reactants is lower than that of the products. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure **10.7.2.2*A***. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the energy of the products is lower than the energy of the reactants, hence is energetically downhill, shown in Figure **10.7.2.2*B***. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

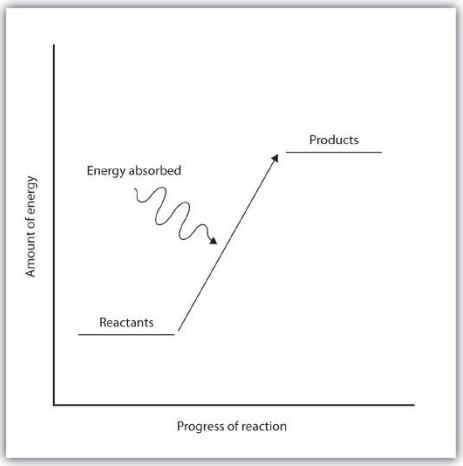


Figure **10.7.2.2*A***: Endothermic Reactions

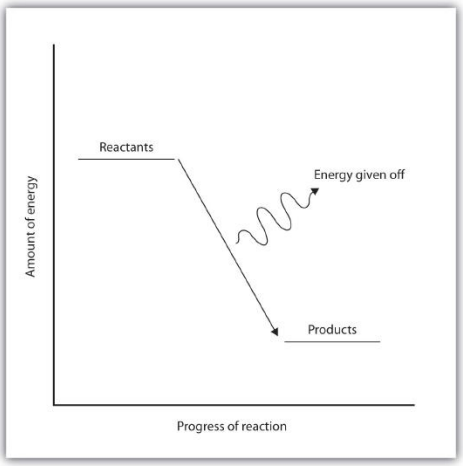


Figure **10.7.2.2*B***: Exothermic Reactions

Table **10.7.2.1**: Endothermic and Exothermic Reactions

Endothermic Reactions	Exothermic Reactions
Heat is absorbed by reactants to form products.	Heat is released.
Heat is absorbed from the surroundings; as a result, the surroundings get cold.	Heat is released by the reaction to surroundings; surroundings feel hot.
ΔH_{rxn} is positive	ΔH_{rxn} is negative
The bonds broken in the reactants are stronger than the bonds formed in the products.	The bonds formed in the products are stronger than the bonds broken in the reactants.
The reactants are lower in energy than the products.	The products are lower in energy than the reactants.
Represented by an "uphill" energy diagram.	Represented by an "downhill" energy diagram

Concept Review Exercises

1. What is the connection between energy and chemical bonds?
2. Why does energy change during the course of a chemical reaction?
3. Two different reactions are performed in two identical test tubes. In reaction A, the test tube becomes very warm as the reaction occurs. In reaction B, the test tube becomes cold. Which reaction is endothermic and which is exothermic? Explain.
4. Classify "burning paper" as endothermic or exothermic processes.

Answers

1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
2. Energy changes because bonds rearrange to make new bonds with different energies.
3. Reaction A is exothermic because heat is leaving the system making the test tube feel hot. Reaction B is endothermic because heat is being absorbed by the system making the test tube feel cold.
4. "Burning paper" is exothermic because burning (also known as combustion) releases heat

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

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10.7.3: Phase Changes

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure **10.7.3.1**.

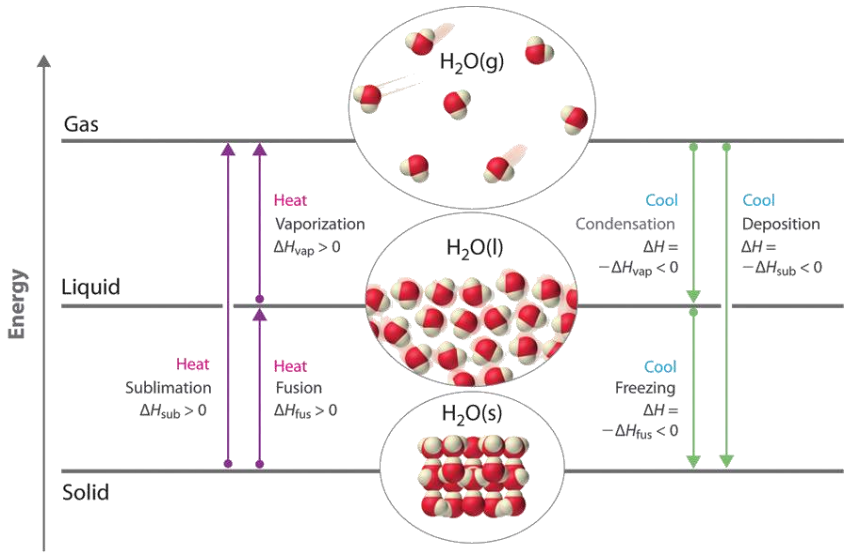


Figure **10.7.3.1**: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. Purple arrows indicate heating from solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure **10.7.3.1**.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table **10.7.3.1**.

Table **10.7.3.1**: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

> *Less energy is needed to allow molecules to move past each other than to separate them totally.*



Figure **10.7.3.2**: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure **10.7.3.2**); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure **10.7.3.1**, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*; this is an application of Hess's law.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{10.7.3.1}$$

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we

exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

The processes on the right side of Figure **10.7.3.1**—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure **10.7.3.3** shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

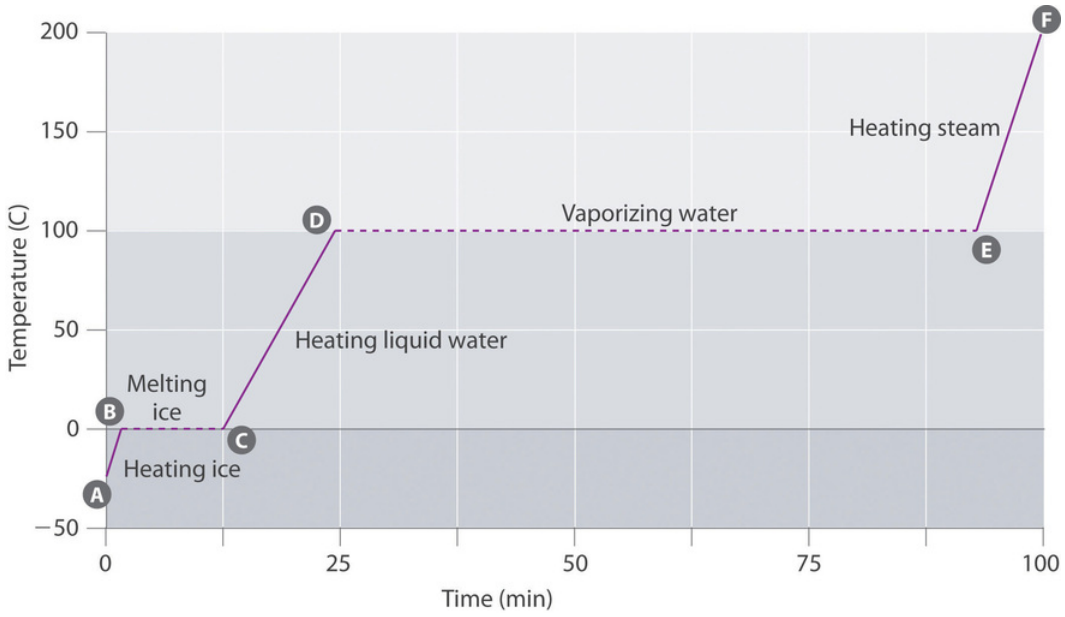


Figure **10.7.3.3**: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up

higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure **10.7.3.3**, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure **10.7.3.3**, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes "bumping" when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or "bump" the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a "boiling chip") in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure **10.7.3.4** plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure **10.7.3.3**, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

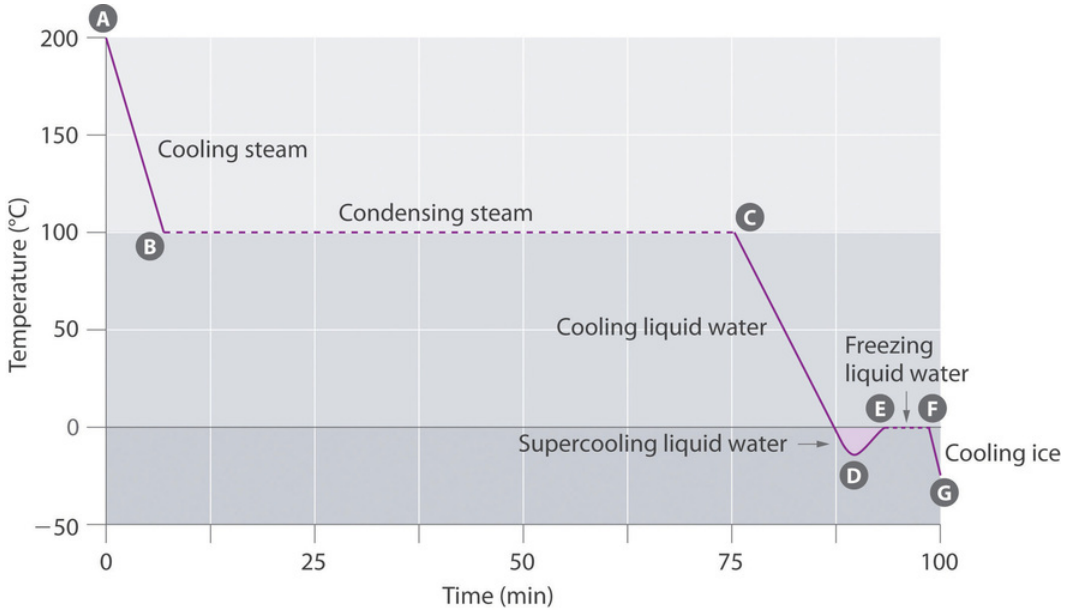


Figure **10.7.3.4**: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.



A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

Example 10.7.3.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$\begin{aligned} q_{ice} &= 50.0g \cdot \frac{1\,mol}{18.02\,g} \cdot 6.01\,kJ/mol \\ &= 16.7\,kJ \end{aligned}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$\begin{aligned} q_{tea} &= -16,700J = 500mL \cdot \frac{1.00\,g}{1\,mL} \cdot 4.184J/(g \bullet °C)\Delta T \\ \Delta T &= -7.98°C = T_f - T_i \\ &= 12.02°C \end{aligned}$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$\begin{aligned} q_{ice} &= -q_{tea} \\ q_{ice} &= m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g \bullet °C) \cdot (T_f - 0.0°C) \\ &= 209.2J/°C \cdot T_f \end{aligned}$$

$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g \bullet °C) \cdot (T_f - 12.02°C) = 2092J/°C \cdot T_f - 25,150J$$

$$209.2J/°C \cdot T_f = -2092J/°C \cdot T_f + 25,150J$$

$$2301.2J/°C \cdot T_f = 25,150J$$

$$T_f = 10.9°C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

? Exercise 10.7.3.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example **10.7.3.1**

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*.

Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

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10.7.4: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure **10.7.4.1**). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure **10.7.4.1**) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

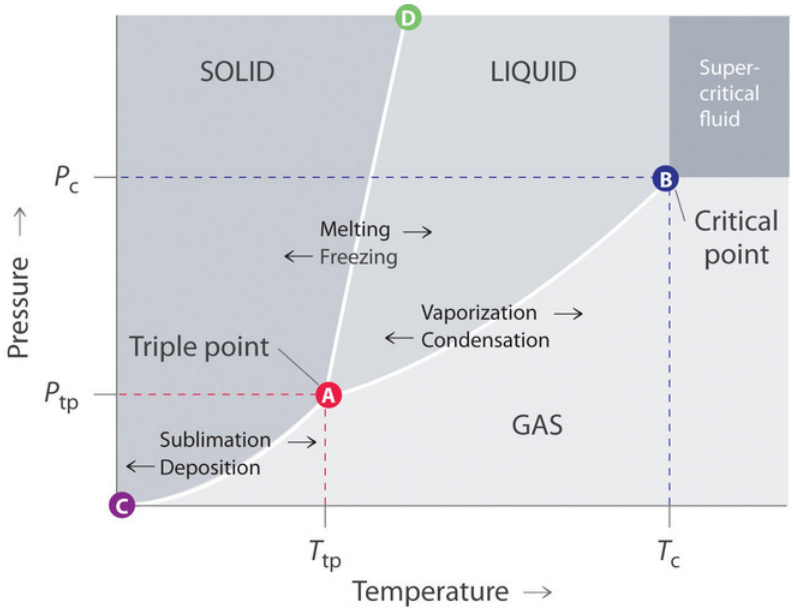


Figure **10.7.4.1**: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure **10.7.4.1**, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure **10.7.4.1**, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a

substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure **10.7.4.2** shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

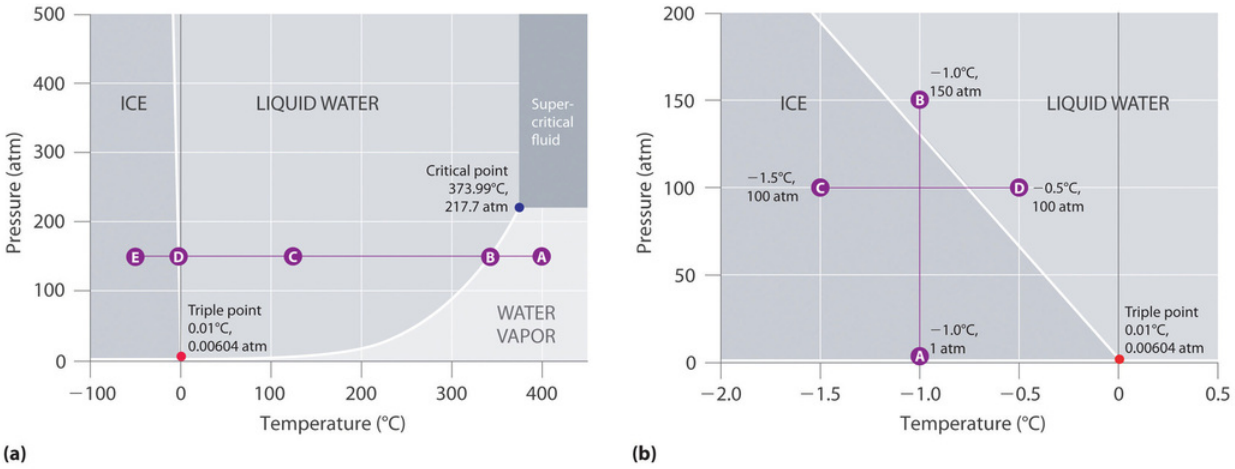


Figure **10.7.4.2**: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example **10.7.4.1**).

The phase diagram for water illustrated in Figure **10.7.4.2***b* shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure **10.7.4.1**; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure **10.7.4.2***b* point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.



Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (P) is the force (F) applied per unit area (A):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where m is the mass and g is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✔ Example 10.7.4.1: Water

Referring to the phase diagram of water in Figure **10.7.4.2**:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure **10.7.4.2**. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure **10.7.4.2**. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

? Exercise 10.7.4.2

Referring to the phase diagram of water in Figure **10.7.4.2**, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure **10.7.4.3**) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

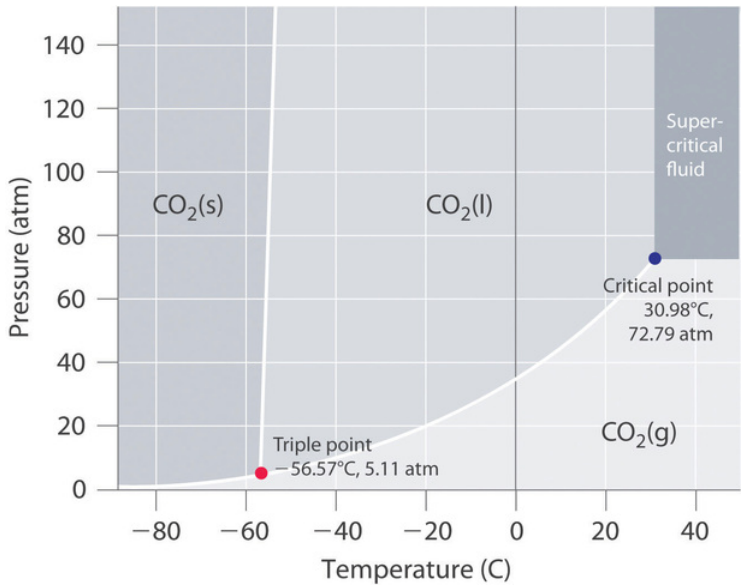


Figure **10.7.4.3**: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure **10.7.4.1**.

Figure **10.7.4.1**: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.



A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

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10.S: Liquids and Intermolecular Forces (Summary)

- intermolecular forces – forces that exist between molecules

11.1: A Molecular Comparison of Gases, Liquids, and Solids

The state of a substance depends on the balance between the kinetic energy of the individual particles (molecules or atoms) and the intermolecular forces. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance and the intermolecular forces try to draw the particles together.

- gases
  - average kinetic energy of the molecules is larger than average energy of attractions between molecules
  - lack of strong attractive forces allows gases to expand
- liquids
  - denser than gases
  - have a definite volume
  - attractive forces not strong enough to keep molecules from moving allowing liquids to hold shape of container
- solids
  - intermolecular forces hold molecules together and keep them from moving
  - not very compressible
  - crystalline – solids with highly ordered structures

Gas, Liquid and Solid

Gas	assumes both the volume and shape of container is compressible diffusion within a gas occurs rapidly flows readily
Liquid	Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Diffusion within a liquid occurs slowly Flows readily
Solid	Retains its own shape and volume Is virtually incompressible Diffusion within a solid occurs extremely slowly Does not flow

- state of substance depends on balance between the kinetic energies of the particles and interparticle energies of attraction
- kinetic energies depends on temperature and tend to keep particles apart and moving
- interparticle attractions draw particles together
- condensed phases – liquids and solids because particles are close together compared to gases
- increase temperature forces molecules to be closer together ® increase in strength of intermolecular forces

11.2: Intermolecular Forces

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold molecules and polyatomic ions together. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as van der Waals forces), and hydrogen bonds.

- intermolecular forces weaker than ionic or covalent bonds
- many properties of liquids reflect strengths of intermolecular forces
- three types of intermolecular forces: dipole-dipole forces, London dispersion forces, and hydrogen-bonding forces
  - also called van der Waals forces
  - less than 15% as strong as covalent or ionic bonds
  - electrostatic in nature, involves attractions between positive and negative species

11.2.1 Ion-Dipole Forces

- Ion-Dipole Force – exists between an ion and partial charge at one end of a polar molecule
- Polar molecules are dipoles
- magnitude of attraction increases as either the charge of ion or magnitude of dipole moment increases

11.2.2 Dipole-Dipole Forces

- dipole-dipole force – exists between neutral polar molecules
- effective only when polar molecules are very close together
- weaker than ion-dipole forces
- for molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity
- increase dipole moment ® increase boiling point

11.2.3 London Dispersion Forces

- - interparticle forces that exist between nonpolar atoms or molecules
  - motion of electrons can create an instantaneous dipole moment
  - molecules have to be very close together
  - polarizability – ease in which the charge distribution in a molecule can be distorted
  - greater polarizability ® more easily electron cloud can be distorted to give momentary dipole
  - larger molecules have greater polarizability
  - London dispersion forces increase with increasing molecular size
  - Dispersion forces increase in strength with increasing molecular weight
  - Molecular shape affects intermolecular attractions
  - greater surface contact ® greater boiling point and London dispersion forces
  - dispersion forces operate between all molecules
  - comparing relative strengths of intermolecular attractions:
  - 1) comparable molecular weights and shapes = equal dispersion forces
    - differences in magnitudes of attractive forces due to differences in strengths of dipole-dipole attractions
    - most polar molecule has strongest attractions
  - 2) differing molecular weights = dispersion forces tend to be the decisive ones
    - differences in magnitudes of attractive forces associated with differences in molecular weights
    - most massive molecular has strongest attractions

11.2.4 Hydrogen Bonding

- hydrogen bonding – special type of intermolecular attraction that exists between the hydrogen atom in a polar bond and an unshared electron pair on a nearby electronegative ion or atom
- hydrogen bond with F, N, and O is polar
- density of ice is lower than that of liquid water
- when water freezes the molecules assume the ordered open arrangement ® makes ice less dense than water
- a given mass of ice has a greater volume than the same mass of water
- structure of ice allows the maximum number of hydrogen bonding interactions to exist

11.2.5 Comparing Intermolecular Forces

- dispersion forces found in all substances
- strengths of forces increase with increases molecular weight and also depend on shape
- dipole-dipole forces add to effect of dispersion forces and found in polar molecules
- hydrogen bonds tend to be strongest intermolecular force

11.3: Some Properties of Liquids

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. Surface tension is the energy required to increase the surface area of a liquid. Surfactants are molecules that reduce

the surface tension of polar liquids like water. Capillary action is the phenomenon in which liquids rise up into a narrow tube called a capillary. The viscosity of a liquid is its resistance to flow.

- two properties of liquids: viscosity and surface tension

11.3.1 Viscosity

- viscosity – resistance of a liquid to flow
- the greater the viscosity the more slowly the liquid flows
- measured by timing how long it takes a certain amount of liquid to flow through a thin tube under gravitational forces
- can also be measured by how long it takes steel spheres to fall through the liquid
- viscosity related to ease with which individual molecules of liquid can move with respect to one another
- depends on attractive forces between molecules, and whether structural features exist to cause molecules to be entangled
- viscosity decreases with increasing temperature

11.3.2 Surface Tension

- surface tension – energy required to increase the surface area of a liquid by a unit amount
- surface tension of water at 20° C is 7.29×10^{-2} J/m^2
- 7.29×10^{-2} J/m^2 must be supplied to increase surface area of a given amount of water by 1 m^2
- cohesive forces – intermolecular forces that bind similar molecules
- adhesive forces – intermolecular forces that bind a substance to a surface
- capillary action – rise of liquids up very narrow tubes

11.4: Phase Changes

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of phase changes, or phase transitions. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are endothermic. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always exothermic.

11.4.1 Energy Changes Accompanying Phase Changes

- phase changes require energy
- phase changes to less ordered state requires energy
- melting process of solid called fusion
- heat of fusion – enthalpy change of melting a solid
- D H_{fus} water = 6.01 kJ/mol
- heat of vaporization – heat needed for vaporization of liquid
- D H_{vap} water = 40.67 kJ/mol
- melting, vaporization, and sublimation are endothermic
- freezing, condensation, and deposition are exothermic

11.4.2 Heating Curves

- heating curve – graph of temperature of system versus the amount of heat added
- used to calculate enthalpy changes
- supercooled water – when water if cooled to a temperature below 0° C

11.4.3 Critical Temperature and Pressure

- critical temperature – highest temperature at which a substance can exist as a liquid
- critical pressure – pressure required to bring about liquefaction at critical temperature
- the greater the intermolecular attractive forces, the more readily gases liquefy ® higher critical temperature
- cannot liquefy a gas by applying pressure if gas is above critical temperature

11.5: Vapor Pressure

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called vaporization or evaporation, generates a vapor pressure above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via condensation. Eventually, a steady state or dynamic equilibrium is reached.

vapor pressure – measures tendency of a liquid to evaporate

11.5.1 Explaining Vapor Pressure on the Molecular Level

- dynamic equilibrium – condition when two opposing processes are occurring simultaneously at equal rates
- vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor states are in dynamic equilibrium

11.5.2 Volatility, Vapor Pressure, and Temperature

- volatile – liquids that evaporate readily
- vapor pressure increases with increasing temperature

11.5.3 Vapor Pressure and Boiling Point

- liquids boil when its vapor pressure equals the external pressure acting on the surface of the liquid
- temperature of boiling increase with increasing external pressure
- normal boiling point – boiling point of a liquid at 1 atm
- higher pressures cause water to boil at higher temperatures

11.6: Phase Diagrams

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a phase diagram, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point.

- phase diagrams – graphical way to summarize conditions under which equilibria exist between the different states of matter
- three important curves:
  - 1) vapor pressure curve of liquid
  - shows equilibrium of liquid and gas phases
  - normal boiling point = point on curve where pressure at 1 atm
  - 2) variation in vapor pressure of solid at it sublimes at different temperatures
  - 3) change in melting point of solid with increasing pressure
  - slopes right as pressure increases
  - higher temperatures needed to melt solids at higher pressures
  - melting point of solid identical to freezing point
    - differ only in temperature direction from which phase change is approached
    - melting point at 1 atm is the normal melting point
- triple point – point at which all three phases are at equilibrium
- gas phase stable at low pressures and high temperatures
- solid phase stable at low temperatures and high pressures
- liquid phase – stable between gas and solids

11.6.1 the Phase diagrams of H_2O and CO_2

- melting point of CO_2 increases with increasing pressure
- melting point of H_2O decreases with increasing pressure
- triple point of H_2O (0.0098° C and 4.58 torr) at lower pressure than CO_2 (-56.4° C and 5.11 atm)
- solid CO_2 does not melt but sublimes
- CO_2 does not have a normal melting point but a normal sublimation point

- CO_2 absorbs energy at ordinary temperatures

11.7: Structure of Solids

A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure. Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array. The smallest repeating unit of a crystal lattice is the unit cell.

- crystalline solid – solid whose atoms, ion, or molecules are ordered in well-defined arrangements
  - flat surfaces or faces that make definite angles
  - regular shapes
- amorphous solid – solid whose particles have no orderly structure
  - lack well-defined faces and shapes
  - mixtures of molecules that do not stack together well
  - large, complicated molecules
  - intermolecular forces vary in strength
  - does not melt at a specific temperature but soften over a temperature range

11.7.1 Unit Cell

- unit cell – repeating unit of a solid
  - crystal lattice – three-dimensional array of points, each representing an identical environment within the crystal
  - three types of cubic unit cell: primitive cubic, body-centered cubic, and face-centered cubic
  - primitive cubic – lattice points at corners only
  - body-centered cubic – lattice points at corners and center
  - face-centered cubic – lattice points at center of each face and at each corner

11.7.2 The Crystal structure of Sodium Chloride

- total cation-to-anion ratio of a unit cell must be the same as that for entire crystal

11.7.3 Close Packing of Spheres

- structures of crystalline solids are those that bring particles in closest contact to maximize the attractive forces
  - most particles that make up solids are spherical
  - two forms of close packing: cubic close packing and hexagonal close packing
  - hexagonal close packing – spheres of the third layer that are placed in line with those of the first layer
  - coordination number – number of particles immediately surrounding a particle in the crystal structure
  - both forms of close packing have coordination number of 12

11.8: Bonding in Solids

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. Metallic solids have unusual properties.

Major Types of Solid

Type of Solid	Forms of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms of molecules	London dispersion, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, methane, sucrose, dry ice
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, quartz
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts
Metallic	atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements

11.8.1 Molecular Solids

- molecular solids – atoms or molecules held together by intermolecular forces
- soft, low melting points
- gases or liquids at room temperature from molecular solids at low temperature
- properties depends on strengths of forces and ability of molecules to pack efficiently in three dimensions
- intermolecular forces that depend on close contact are not as effective

11.8.2 Covalent-Network Solids

- covalent-network solids – atoms held together in large networks or chains by covalent bonds
- hard, high melting points

11.8.3 Ionic Solids

- ionic solids – ions held together by ionic bonds
- strength depends on charges of ions
- structure of ionic solids depends on charges and relative sizes of ions

11.8.4 Metallic Solids

- metallic solids – metal atoms
- usually have hexagonal close-packed, cubic close-packed, or body-centered-cubic structures
- each atom has 8 or 12 adjacent atoms
- bonding due to valence electrons that are delocalized throughout entire solid
- strength of bonding increases as number of electrons available for bonding increases
- mobility of electrons make metallic solids good conductors of heat and electricity

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CHAPTER OVERVIEW

11: The Chemical Equation

A chemical equation is a concise description of a chemical reaction. Proper chemical equations are balanced.

Learning Objectives

- Define *chemical equation*.
- Identify the parts of a chemical equation.

A chemical reaction expresses a chemical change. For example, one chemical property of hydrogen is that it will react with oxygen to make water. We can write that as follows:

$$\text{hydrogen reacts with oxygen to make water}$$

We can represent this chemical change more succinctly as:

$$\text{hydrogen} + \text{oxygen} \rightarrow \text{water}$$

where the + sign means that the two substances interact chemically with each other and the → symbol implies that a chemical reaction takes place. But substances can also be represented by chemical formulas. Remembering that hydrogen and oxygen both exist as diatomic molecules, we can rewrite our chemical change as:

$$\mathrm{H_2 + O_2 \longrightarrow H_2O}$$

This is an example of a chemical equation, which is a concise way of representing a **chemical reaction**. The initial substances are called **reactants** and the final substances are called **products**.

Unfortunately, it is also an *incomplete* chemical equation. The law of conservation of matter says that matter cannot be created or destroyed. In chemical equations, the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the products. If we count the number of hydrogen atoms in the reactants and products, we find two hydrogen atoms. But if we count the number of oxygen atoms in the reactants and products, we find that there are two oxygen atoms in the reactants, but only one oxygen atom in the products.

What can we do? Can we change the subscripts in the formula for water so that it has two oxygen atoms in it? No—you *cannot* change the formulas of individual substances, because the chemical formula for a given substance is characteristic of that substance. What you *can* do, however, is to change the number of molecules that react or are produced. We do this one element at a time, going from one side of the reaction to the other, changing the number of molecules of a substance until all elements have the same number of atoms on each side.

To accommodate the two oxygen atoms as reactants, let us assume that we have two water molecules as products:

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

The 2 in front of the formula for water is called a **coefficient**. Now there are the same number of oxygen atoms in the reactants as there are in the product. But in satisfying the need for the same number of oxygen atoms on both sides of the reaction, we have also changed the number of hydrogen atoms on the product side, so the number of hydrogen atoms is no longer equal. No problem, simply go back to the reactant side of the equation, and add a coefficient in front of the H_2. The coefficient that works is 2:

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

There are now four hydrogen atoms in the reactants and also four atoms of hydrogen in the product. There are two oxygen atoms in the reactants and two atoms of oxygen in the product. The law of conservation of matter has been satisfied. When the reactants and products of a chemical equation have the same number of atoms of all elements present, we say that an equation is **balanced**. All proper chemical equations are balanced. If a substance does not have a coefficient written in front of it, it is assumed to be 1. Also,

the convention is to use all whole numbers when balancing chemical equations. This sometimes makes us do a bit more "back and forth" work when balancing a chemical equation.

Example 11.1

Write and balance the chemical equation for each given chemical reaction.

1. Hydrogen and chlorine react to make HCl
2. Ethane, $\mathrm{C_2H_6}$, reacts with oxygen to make carbon dioxide and water.

Solution

1. Let us start by simply writing a chemical equation in terms of the formulas of the substances, remembering that both elemental hydrogen and chlorine are diatomic:

$$\mathrm{H_2 + Cl_2 \longrightarrow HCl}$$

There are two hydrogen atoms and two chlorine atoms in the reactants and one of each atom in the product. We can fix this by including the coefficient 2 on the product side:

$$\mathrm{H_2 + Cl_2 \longrightarrow 2\,HCl}$$

Now there are two hydrogen atoms and two chlorine atoms on both sides of the chemical equation, so it is balanced.

2. Start by writing the chemical equation in terms of the substances involved:

$$\mathrm{C_2H_6 + O_2 \longrightarrow CO_2 + H_2O}$$

We have two carbon atoms on the left, so we need two carbon dioxide molecules on the product side, so that each side has two carbon atoms; that element is balanced. We have six hydrogen atoms in the reactants, so we need six hydrogen atoms in the products. We can get this by having three water molecules:

$$\mathrm{C_2H_6 + O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

Now we have seven oxygen atoms in the products (four from the CO_2 and three from the H_2O). This means we need seven oxygen atoms in the reactants. However, because oxygen is a diatomic molecule, we can only get an even number of oxygen atoms at a time. We can achieve this by multiplying the other coefficients by 2:

$$\mathrm{2\,C_2H_6 + O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

By multiplying everything else by 2, we do not unbalance the other elements, and we now get an even number of oxygen atoms in the product—14. We can get 14 oxygen atoms on the reactant side by having 7 oxygen molecules:

$$\mathrm{2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

As a check, recount everything to determine that each side has the same number of atoms of each element. This chemical equation is now balanced.

Exercise 11.1

Write and balance the chemical equation that represents nitrogen and hydrogen reacting to produce ammonia, NH_3.

Answer

\[\ce{N2 + 3H2 → 2NH3 \nonumber \nonumber \]

Many chemical equations also include phase labels for the substances: (s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for aqueous (i.e., dissolved in water). Special conditions, such as temperature, may also be listed above the arrow. For example,

$$\mathrm{2\,NaHCO_3\,(s) \overset{200^\circ C}{\rightarrow} Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)}$$

Key Takeaways

- A chemical equation is a concise description of a chemical reaction.
- Proper chemical equations are balanced.

11.1: Introduction
11.2: Types of Chemical Reactions - Single and Double Displacement Reactions
11.3: Types of Chemical Reactions - Single and Double Displacement Reactions
11.4: Ionic Equations - A Closer Look
11.5: Composition, Decomposition, and Combustion Reactions
11.6: Stoichiometry
11.7: The Mole
11.7.1: The Mole in Chemical Reactions

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11.1: Introduction

At Contrived State University in Anytown, Ohio, a new building was dedicated in March 2010 to house the College of Education. The 100,000-square-foot building has enough office space to accommodate 86 full-time faculty members and 167 full-time staff. In a fit of monetary excess, the university administration offered to buy new furniture (desks and chairs) and computer workstations for all faculty and staff members moving into the new building. However, to save on long-term energy and materials costs, the university offered to buy only 1 laser printer per 10 employees, with the plan to network the printers together.



Figure **11.1.1** Outfitting a New Building. Source: Photo courtesy of Benjamin Benschneider, Cleveland State University.

How many laser printers did the administration have to buy? It is rather simple to show that 26 laser printers are needed for all the employees. However, what if a chemist was calculating quantities for a chemical reaction? Interestingly enough, similar calculations can be performed for chemicals as well as laser printers. In filling a new office building with furniture and equipment, managers do calculations similar to those performed by scientists doing chemical reactions.

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11.2: Types of Chemical Reactions - Single and Double Displacement Reactions

Learning Objectives

- Recognize chemical reactions as single-replacement reactions and double-replacement reactions.
- Use the periodic table, an activity series, or solubility rules to predict whether single-replacement reactions or double-replacement reactions will occur.

Up until now, we have presented chemical reactions as a topic, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be.

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. Presented below:

$$2\,HCl\,(aq) + Zn\,(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

is an example of a single-replacement reaction. The hydrogen atoms in **HCl** are replaced by **Zn** atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2\,NaCl\,(aq) + F_2\,(g) \longrightarrow 2\,NaF\,(s) + Cl_2\,(g)$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

Not all proposed single-replacement reactions will occur between two given reactants. This is most easily demonstrated with fluorine, chlorine, bromine, and iodine. Collectively, these elements are called the *halogens* and are in the next-to-last column on the periodic table (Figure **11.2.1**). The elements on top of the column will replace the elements below them on the periodic table, but not the other way around. Thus, the reaction represented by

$$CaI_2\,(s) + Cl_2\,(g) \longrightarrow CaCl_2\,(s) + I_2\,(s)$$

will occur; but the reaction

$$CaF_2\,(s) + Br_2(\ell) \longrightarrow CaBr_2\,(s) + F_2\,(g)$$

will not, because bromine is below fluorine on the periodic table. This is just one of many ways the periodic table helps us to understand chemistry.

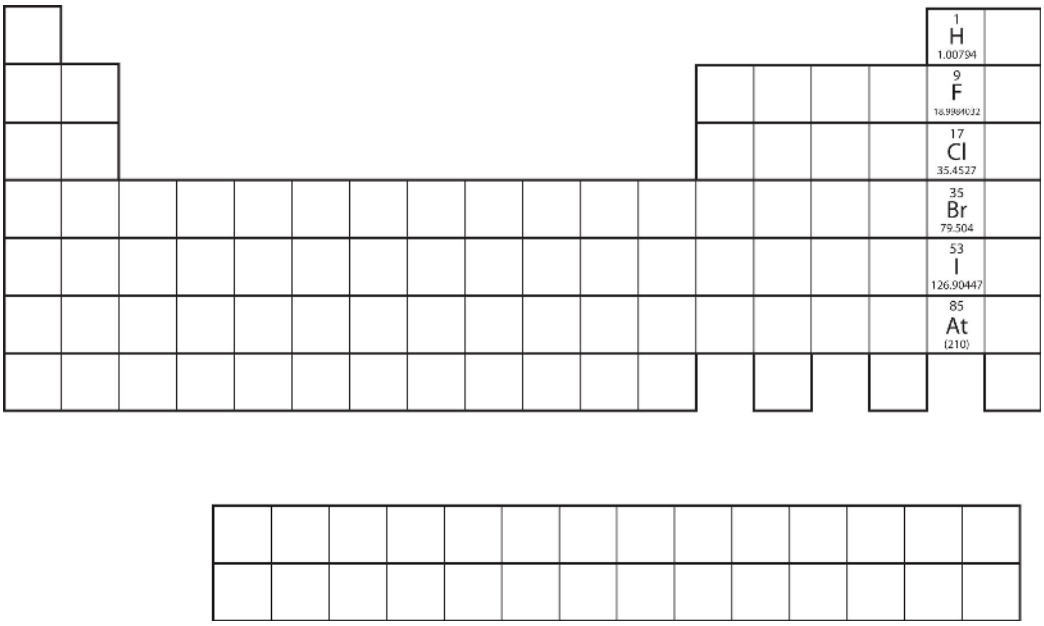


Figure 11.2.1: Halogens on the Periodic Table. The halogens are the elements in the next-to-last column on the periodic table.

Example 11.2.1

Will a single-replacement reaction occur? If so, identify the products.

a. $MgCl_2 + I_2 \rightarrow ?$
b. $CaBr_2 + F_2 \rightarrow ?$

Solution

a. Because iodine is below chlorine on the periodic table, a single-replacement reaction will not occur.
b. Because fluorine is above bromine on the periodic table, a single-replacement reaction will occur, and the products of the reaction will be CaF_2 and Br_2.

Exercise 11.2.1

Will a single-replacement reaction occur? If so, identify the products.

$$\mathbf{FeI_2 + Cl_2 \longrightarrow}$$

Answer

Yes; $FeCl_2$ and I_2

Chemical reactivity trends are easy to predict when replacing anions in simple ionic compounds—simply use their relative positions on the periodic table. However, when replacing the cations, the trends are not as straightforward. This is partly because there are so many elements that can form cations; an element in one column on the periodic table may replace another element nearby, or it may not. A list called the **activity series** does the same thing the periodic table does for halogens: it lists the elements that will replace elements below them in single-replacement reactions. A simple activity series is shown below.

Activity Series for Cation Replacement in Single-Replacement Reactions

- Li
- K
- Ba
- Sr
- Ca

- Na
- Mg
- Al
- Mn
- Zn
- Cr
- Fe
- Ni
- Sn
- Pb
- H_2
- Cu
- Hg
- Ag
- Pd
- Pt
- Au

Using the activity series is similar to using the positions of the halogens on the periodic table. An element on top will replace an element below it in compounds undergoing a single-replacement reaction. Elements will not replace elements above them in compounds.

Example 11.2.2

Use the activity series to predict the products, if any, of each equation.

1. $FeCl_2 + Zn \rightarrow ?$
2. $HNO_3 + Au \rightarrow ?$

Solution

1. Because zinc is above iron in the activity series, it will replace iron in the compound. The products of this single-replacement reaction are $ZnCl_2$ and Fe.
2. Gold is below hydrogen in the activity series. As such, it will not replace hydrogen in a compound with the nitrate ion. No reaction is predicted.

Exercise 11.2.2

Use the activity series to predict the products, if any, of this equation.

$$AlPO_4 + Mg \longrightarrow$$

Answer

$Mg_3(PO_4)_2$ and Al

A **double-replacement reaction** occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products. An example is

$$CuCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,AgCl\,(s)$$

There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either perspective should allow you to predict the proper products, as long as you pair a cation with an anion, and not a cation with a cation or an anion with an anion.

Example 11.2.3

Predict the products of this double-replacement equation:

$$\mathrm{BaCl_2 + Na_2SO_4 \longrightarrow}$$

Solution

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and NaCl.

Exercise 11.2.3

Predict the products of this double-replacement equation:

$$\mathrm{KBr + AgNO_3 \longrightarrow}$$

Answer

KNO_3 and AgBr

Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. However, there is one type of double-replacement reaction that we can predict: the precipitation reaction. A **precipitation reaction** occurs when two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve; this new compound falls out of solution as a solid **precipitate.** The formation of a solid precipitate is the driving force that makes the reaction proceed.

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table **11.2.1** lists some general solubility rules. We need to consider each ionic compound (both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (aq) label with it, indicating that it dissolves. If a compound is not soluble, we use the (s) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table **11.2.1**: Some Useful Solubility Rules (soluble)

These compounds generally dissolve in water (are soluble):	Exceptions:
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+	None
All compounds of NO_3^- and $C_2H_3O_2^-$	None
Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table **11.2.2**: Some Useful Solubility Rules (insoluble)

These compounds generally do not dissolve in water (are insoluble):	Exceptions:
Compounds of CO_3^{2-} and PO_4^{3-}	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+
Compounds of OH^-	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate

ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$Na_2SO_4\,(aq) + SrCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + SrSO_4\,(s)$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 11.2.2).



Figure 11.2.2: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, http://commons.wikimedia.org/wiki/File:Copper_solution.jpg(opens in new window).

Example 11.2.4

Will a double-replacement reaction occur? If so, identify the products.

1. $Ca(NO_3)_2$ + KBr → ?
2. NaOH + $FeCl_2$ → ?

Solution

1. According to the solubility rules, both $Ca(NO_3)_2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr_2$ and KNO_3. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.
2. According to the solubility rules, both NaOH and $FeCl_2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)_2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)_2$ is not. Therefore, a reaction would occur, and $Fe(OH)_2$(s) would precipitate out of solution. The balanced chemical equation is

$$2\,NaOH\,(aq) + FeCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + Fe(OH)_2\,(s)$$

Exercise 11.2.4

$$Sr(NO_3)_2 + KCl \longrightarrow$$

Answer

No reaction; all possible products are soluble.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- The periodic table or an activity series can help predict whether single-replacement reactions occur.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.
- A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.
- Solubility rules are used to predict whether some double-replacement reactions will occur.

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11.3: Types of Chemical Reactions - Single and Double Displacement Reactions

Learning Objectives

- Recognize chemical reactions as single-replacement reactions and double-replacement reactions.
- Use the periodic table, an activity series, or solubility rules to predict whether single-replacement reactions or double-replacement reactions will occur.

Up until now, we have presented chemical reactions as a topic, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be.

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. Presented below:

$$2\,HCl\,(aq) + Zn\,(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

is an example of a single-replacement reaction. The hydrogen atoms in **HCl** are replaced by **Zn** atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2\,NaCl\,(aq) + F_2\,(g) \longrightarrow 2\,NaF\,(s) + Cl_2\,(g)$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

Not all proposed single-replacement reactions will occur between two given reactants. This is most easily demonstrated with fluorine, chlorine, bromine, and iodine. Collectively, these elements are called the *halogens* and are in the next-to-last column on the periodic table (Figure **11.3.1**). The elements on top of the column will replace the elements below them on the periodic table, but not the other way around. Thus, the reaction represented by

$$CaI_2\,(s) + Cl_2\,(g) \longrightarrow CaCl_2\,(s) + I_2\,(s)$$

will occur; but the reaction

$$CaF_2\,(s) + Br_2(\ell) \longrightarrow CaBr_2\,(s) + F_2\,(g)$$

will not, because bromine is below fluorine on the periodic table. This is just one of many ways the periodic table helps us to understand chemistry.

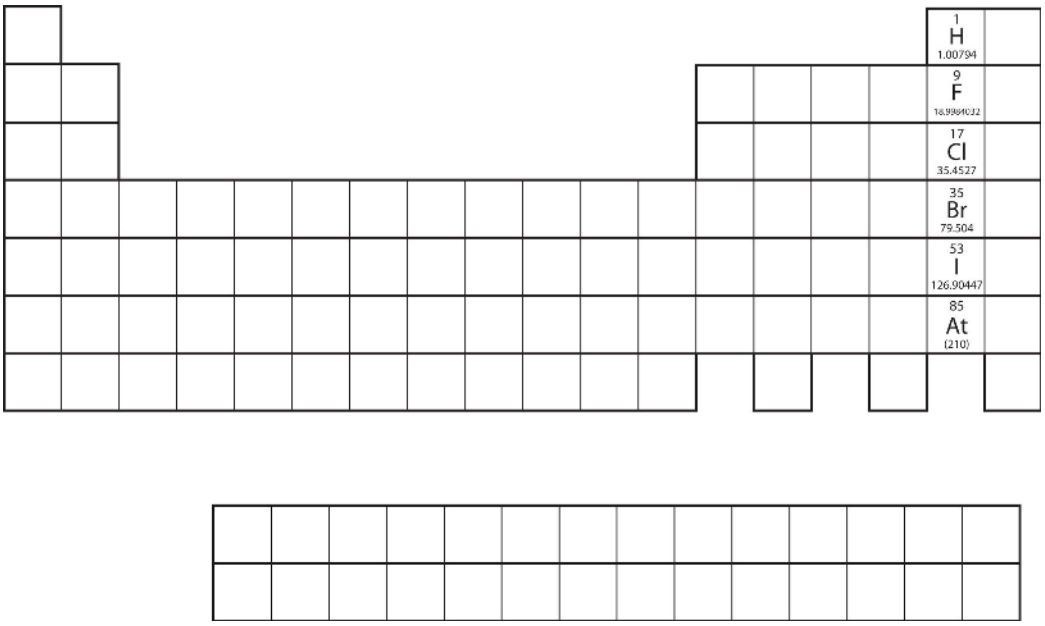


Figure **11.3.1**: Halogens on the Periodic Table. The halogens are the elements in the next-to-last column on the periodic table.

Example 11.3.1

Will a single-replacement reaction occur? If so, identify the products.

a. $MgCl_2 + I_2 \rightarrow ?$
b. $CaBr_2 + F_2 \rightarrow ?$

Solution

a. Because iodine is below chlorine on the periodic table, a single-replacement reaction will not occur.
b. Because fluorine is above bromine on the periodic table, a single-replacement reaction will occur, and the products of the reaction will be CaF_2 and Br_2.

Exercise 11.3.1

Will a single-replacement reaction occur? If so, identify the products.

$$\mathbf{FeI_2 + Cl_2 \longrightarrow}$$

Answer

Yes; $FeCl_2$ and I_2

Chemical reactivity trends are easy to predict when replacing anions in simple ionic compounds—simply use their relative positions on the periodic table. However, when replacing the cations, the trends are not as straightforward. This is partly because there are so many elements that can form cations; an element in one column on the periodic table may replace another element nearby, or it may not. A list called the **activity series** does the same thing the periodic table does for halogens: it lists the elements that will replace elements below them in single-replacement reactions. A simple activity series is shown below.

Activity Series for Cation Replacement in Single-Replacement Reactions

- Li
- K
- Ba
- Sr
- Ca

- Na
- Mg
- Al
- Mn
- Zn
- Cr
- Fe
- Ni
- Sn
- Pb
- H_2
- Cu
- Hg
- Ag
- Pd
- Pt
- Au

Using the activity series is similar to using the positions of the halogens on the periodic table. An element on top will replace an element below it in compounds undergoing a single-replacement reaction. Elements will not replace elements above them in compounds.

Example 11.3.2

Use the activity series to predict the products, if any, of each equation.

1. $FeCl_2 + Zn \rightarrow ?$
2. $HNO_3 + Au \rightarrow ?$

Solution

1. Because zinc is above iron in the activity series, it will replace iron in the compound. The products of this single-replacement reaction are $ZnCl_2$ and Fe.
2. Gold is below hydrogen in the activity series. As such, it will not replace hydrogen in a compound with the nitrate ion. No reaction is predicted.

Exercise 11.3.2

Use the activity series to predict the products, if any, of this equation.

$$AlPO_4 + Mg \longrightarrow$$

Answer

$Mg_3(PO_4)_2$ and Al

A **double-replacement reaction** occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products. An example is

$$CuCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,AgCl\,(s)$$

There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either perspective should allow you to predict the proper products, as long as you pair a cation with an anion, and not a cation with a cation or an anion with an anion.

Example 11.3.3

Predict the products of this double-replacement equation:

$$\mathrm{BaCl_2 + Na_2SO_4 \longrightarrow}$$

Solution

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and NaCl.

Exercise 11.3.3

Predict the products of this double-replacement equation:

$$\mathrm{KBr + AgNO_3 \longrightarrow}$$

Answer

KNO_3 and AgBr

Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. However, there is one type of double-replacement reaction that we can predict: the precipitation reaction. A **precipitation reaction** occurs when two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve; this new compound falls out of solution as a solid **precipitate.** The formation of a solid precipitate is the driving force that makes the reaction proceed.

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table **11.3.1** lists some general solubility rules. We need to consider each ionic compound (both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (aq) label with it, indicating that it dissolves. If a compound is not soluble, we use the (s) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table **11.3.1**: Some Useful Solubility Rules (soluble)

These compounds generally dissolve in water (are soluble):	Exceptions:
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+	None
All compounds of NO_3^- and $C_2H_3O_2^-$	None
Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table **11.3.2**: Some Useful Solubility Rules (insoluble)

These compounds generally do not dissolve in water (are insoluble):	Exceptions:
Compounds of CO_3^{2-} and PO_4^{3-}	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+
Compounds of OH^-	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate

ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$Na_2SO_4\,(aq) + SrCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + SrSO_4\,(s)$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 11.3.2).



Figure 11.3.2: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, http://commons.wikimedia.org/wiki/File:Copper_solution.jpg(opens in new window).

Example 11.3.4

Will a double-replacement reaction occur? If so, identify the products.

1. $Ca(NO_3)_2$ + KBr → ?
2. NaOH + $FeCl_2$ → ?

Solution

1. According to the solubility rules, both $Ca(NO_3)_2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr_2$ and KNO_3. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.
2. According to the solubility rules, both NaOH and $FeCl_2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)_2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)_2$ is not. Therefore, a reaction would occur, and $Fe(OH)_2$(s) would precipitate out of solution. The balanced chemical equation is

$$2\,NaOH\,(aq) + FeCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + Fe(OH)_2\,(s)$$

Exercise 11.3.4

$$Sr(NO_3)_2 + KCl \longrightarrow$$

Answer

No reaction; all possible products are soluble.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- The periodic table or an activity series can help predict whether single-replacement reactions occur.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.
- A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.
- Solubility rules are used to predict whether some double-replacement reactions will occur.

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11.4: Ionic Equations - A Closer Look

Learning Objectives

- Write ionic equations for chemical reactions between ionic compounds.
- Write net ionic equations for chemical reactions between ionic compounds.

For single-replacement and double-replacement reactions, many of the reactions included ionic compounds—compounds between metals and nonmetals, or compounds that contained recognizable polyatomic ions. Now, we take a closer look at reactions that include ionic compounds.

One important aspect about ionic compounds that differs from molecular compounds has to do with dissolution in a liquid, such as water. When molecular compounds, such as sugar, dissolve in water, the individual molecules drift apart from each other. When ionic compounds dissolve, *the ions physically separate from each other*. We can use a chemical equation to represent this process—for example, with NaCl:

$$\mathrm{NaCl\,(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+\,(aq) + Cl^-\,(aq)}$$

When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure **11.4.1**). This process is called **dissociation;** we say that the ions *dissociate*.

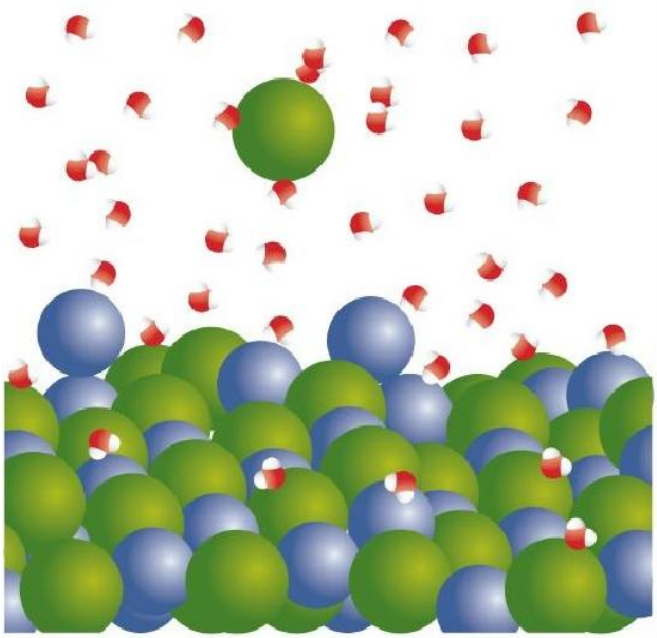


Figure **11.4.1** Ionic Solutions. When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.

All ionic compounds that dissolve behave this way. This behavior was first suggested by the Swedish chemist Svante August Arrhenius [1859–1927] as part of his PhD dissertation in 1884. Interestingly, his PhD examination team had a hard time believing that ionic compounds would behave like this, so they gave Arrhenius a barely passing grade. Later, this work was cited when Arrhenius was awarded the Nobel Prize in Chemistry. Keep in mind that when the ions separate, *all* the ions separate. Thus, when $CaCl_2$ dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from one another:

$$CaCl_2(s) \overset{H_2O}{\rightarrow} Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)$$

$$CaCl_2(s) \overset{H_2O}{\rightarrow} Ca^{2+}(aq) + 2Cl^-(aq)$$

That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions), and they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. Polyatomic ions also retain their overall identity when they are dissolved.

Example 11.4.1

Write the chemical equation that represents the dissociation of each ionic compound.

1. KBr
2. Na_2SO_4

Solution

1. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$
2. Not only do the two sodium ions go their own way, but the sulfate ion stays together as the sulfate ion. The dissolving equation is $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

Exercise 11.4.1

Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Answer

$(NH_4)_2S(s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$

When chemicals in solution react, the proper way of writing the chemical formulas of the dissolved ionic compounds is in terms of the dissociated ions, not the complete ionic formula. A **complete ionic equation** is a chemical equation in which the dissolved ionic compounds are written as separated ions. Solubility rules are very useful in determining which ionic compounds are dissolved and which are not. For example, when NaCl(aq) reacts with $AgNO_3$(aq) in a double-replacement reaction to precipitate AgCl(s) and form $NaNO_3$(aq), the complete ionic equation includes NaCl, $AgNO_3$, and $NaNO_3$ written as separate ions:

$$\mathrm{Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)}$$

This is more representative of what is occurring in the solution.

Example 11.4.1

Write the complete ionic equation for each chemical reaction.

1. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$
2. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

1. The complete ionic equation is $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. The complete ionic equation is $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Exercise 11.4.1

Write the complete ionic equation for

$$\mathrm{CaCl_2(aq) + Pb(NO_3)_2(aq) \longrightarrow Ca(NO_3)_2(aq) + PbCl_2(s)}$$

Answer

$Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$

You may notice that in a complete ionic equation, some ions do not change their chemical form; they stay exactly the same on the reactant and product sides of the equation. For example, in

$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

the $Ag^+(aq)$ and $Cl^-(aq)$ ions become $AgCl(s)$, but the $Na^+(aq)$ ions and the $NO_3^-(aq)$ ions stay as $Na^+(aq)$ ions and $NO_3^-(aq)$ ions. These two ions are examples of spectator ions—ions that do nothing in the overall course of a chemical reaction. They are present, but they do not participate in the overall chemistry. It is common to cancel spectator ions (something also done with algebraic quantities) on the opposite sides of a chemical equation:

$$\cancel{Na^+(aq)} + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-(aq)} \rightarrow AgCl(s) + \cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}$$

What remains when the spectator ions are removed is called the **net ionic equation**, which represents the actual chemical change occurring between the ionic compounds:

$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

It is important to reiterate that the spectator ions are still present in solution, but they do not experience any net chemical change, so they are not written in a net ionic equation.

Example 11.4.1

Write the net ionic equation for each chemical reaction.

1. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Solution

1. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{K^+(aq)} + Br^-(aq) + Ag^+(aq) + \cancel{C_2H_3O_2^-(aq)} \rightarrow K^+(aq) + \cancel{C_2H_3O_2^-(aq)} + AgBr(s)$$

The net ionic equation is

$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$$

2. In the second equation, the $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{Mg^{2+}(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + \cancel{2NO_3^-(aq)} \rightarrow Mg^{2+}(aq) + \cancel{2NO_3^-(aq)} + BaSo_4(s)$$

The net ionic equation is

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Exercise 11.4.1

Write the net ionic equation for

$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

Chemistry is Everywhere: Soluble and Insoluble Ionic Compounds

The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound that can be dissolved in a sample of water. For example, you can dissolve a

maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water. We consider **NaCl** soluble but **AgCl** insoluble.

One place where solubility is important is in the tank-type water heater found in many homes in the United States. Domestic water frequently contains small amounts of dissolved ionic compounds, including calcium carbonate ($CaCO_3$). However, $CaCO_3$ has the relatively unusual property of being less soluble in hot water than in cold water. So as the water heater operates by heating water, $CaCO_3$ can precipitate if there is enough of it in the water. This precipitate, called *limescale*, can also contain magnesium compounds, hydrogen carbonate compounds, and phosphate compounds. The problem is that too much limescale can impede the function of a water heater, requiring more energy to heat water to a specific temperature or even blocking water pipes into or out of the water heater, causing dysfunction.



Figure **11.4.2** Tank water heater © Thinkstock. Most homes in the United States have a tank-type water heater like this one.

Another place where solubility versus insolubility is an issue is the Grand Canyon. We usually think of rock as insoluble. But it is actually ever so slightly soluble. This means that over a period of about two billion years, the Colorado River carved rock from the surface by slowly dissolving it, eventually generating a spectacular series of gorges and canyons. And all because of solubility!



Figure **11.4.3**: The Grand Canyon was formed by water running through rock for billions of years, very slowly dissolving it. Note the Colorado River is still present in the lower part of the photo. (Sonaal Bangera via unsplash)

Key Takeaways

- Ionic compounds that dissolve separate into individual ions.
- Complete ionic equations show dissolved ionic solids as separated ions.
- Net ionic equations show only the ions and other substances that change in a chemical reaction.

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11.5: Composition, Decomposition, and Combustion Reactions

Learning Objectives

- Recognize composition, decomposition, and combustion reactions.
- Predict the products of a combustion reaction.

Three classifications of chemical reactions will be reviewed in this section. Predicting the products in some of them may be difficult, but the reactions are still easy to recognize.

A **composition reaction** (sometimes also called a *combination reaction* or a *synthesis reaction*) produces a single substance from multiple reactants. A single substance as a product is the key characteristic of the composition reaction. There may be a coefficient other than one for the substance, but if the reaction has only a single substance as a product, it can be called a composition reaction. In the reaction

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

water is produced from hydrogen and oxygen. Although there are two molecules of water being produced, there is only one substance—water—as a product. So this is a composition reaction.

A **decomposition reaction** starts from a single substance and produces more than one substance; that is, it decomposes. The key characteristics of a decomposition reaction are: one substance as a reactant and more than one substance as the products. For example, in the decomposition of sodium hydrogen carbonate (also known as sodium bicarbonate):

$$2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O(\ell)$$

sodium carbonate, carbon dioxide, and water are produced from the single substance sodium hydrogen carbonate.

Composition and decomposition reactions are difficult to predict; however, they should be easy to recognize.

Example 11.5.1: Identifying Reactions

Identify each equation as a composition reaction, a decomposition reaction, or neither.

a. $Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$
b. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
c. $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4\,H_2O + N_2$

Solution

a. In this equation, two substances combine to make a single substance. This is a composition reaction.
b. Two different substances react to make two new substances. This does not fit the definition of either a composition reaction or a decomposition reaction, so it is neither. In fact, you may recognize this as a double-replacement reaction.
c. A single substance reacts to make multiple substances. This is a decomposition reaction.

Exercise 11.5.1

Identify the equation as a composition reaction, a decomposition reaction, or neither.

$$C_3H_8 \longrightarrow C_3H_4 + 2\,H_2$$

Answer

decomposition

A **combustion reaction** occurs when a reactant combines with oxygen, many times from the atmosphere, to produce oxides of all other elements as products; any nitrogen in the reactant is converted to elemental nitrogen, N_2. Many reactants, called *fuels*,

contain mostly carbon and hydrogen atoms, reacting with oxygen to produce CO_2 and H_2O. For example, the balanced chemical equation for the combustion of methane, CH_4, is as follows:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

Kerosene can be approximated with the formula $\mathrm{C_{12}H_{26}}$, and its combustion equation is:

$$\mathrm{2\,C_{12}H_{26} + 37\,O_2 \longrightarrow 24\,CO\text{-}2 + 26\,H_2O}$$

Sometimes fuels contain oxygen atoms, which must be counted when balancing the chemical equation. One common fuel is ethanol, $\mathrm{C_2H_5OH}$, whose combustion equation is:

$$\mathrm{C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

If nitrogen is present in the original fuel, it is converted to $\mathrm{N_2}$, not to a nitrogen-oxygen compound. Thus, for the combustion of the fuel dinitroethylene, whose formula is $\mathrm{C_2H_2N_2O_4}$, we have:

$$\mathrm{2\,C_2H_2N_2O_4 + O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 2\,N_2}$$

Example 11.5.2: Combustion Reactions

Complete and balance each combustion equation.

1. the combustion of propane ($\mathrm{C_3H_8}$)
2. the combustion of ammonia ($\mathrm{NH_3}$)

Solution

1. The products of the reaction are CO_2 and H_2O, so our unbalanced equation is

   $$\mathrm{C_3H_8 + O_2 \longrightarrow CO_2 + H_2O}$$

   Balancing (and you may have to go back and forth a few times to balance this), we get

   $$\mathrm{C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O}$$

2. The nitrogen atoms in ammonia will react to make N_2, while the hydrogen atoms will react with O_2 to make H_2O:

   $$\mathrm{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

   To balance this equation without fractions (which is the convention), we get

   $$\mathrm{4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O}$$

Exercise 11.5.2

Complete and balance the combustion equation for cyclopropanol (\ce{C3H6O}\)).

Answer

$$\mathrm{C_3H_6O + 4\,O_2 \longrightarrow 3\,CO_2 + 3\,H_2O}$$



Figure **11.5.1** A 20 lb (9.1 kg) steel propane cylinder.

Key Takeaways

- A composition reaction produces a single substance from multiple reactants.
- A decomposition reaction produces multiple products from a single reactant.
- Combustion reactions are the combination of some compound with oxygen to make oxides of the other elements as products (although nitrogen atoms react to make N_2).

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11.6: Stoichiometry

Learning Objectives

- Define *stoichiometry*.
- Relate quantities in a balanced chemical reaction on a molecular basis.

Consider a classic recipe for pound cake: 1 pound of eggs, 1 pound of butter, 1 pound of flour, and 1 pound of sugar. (That's why it's called "pound cake.") If you have 4 pounds of butter, how many pounds of sugar, flour, and eggs do you need? You would need 4 pounds each of sugar, flour, and eggs.

Now suppose you have 1.00 g H_2. If the chemical reaction follows the balanced chemical equation

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

then what mass of oxygen do you need to make water?

Curiously, this chemical reaction question is very similar to the pound cake question. Both of them involve relating a quantity of one substance to a quantity of another substance or substances. The relating of one chemical substance to another using a balanced chemical reaction is called **stoichiometry**. Using stoichiometry is a fundamental skill in chemistry; it greatly broadens your ability to predict what will occur and, more importantly, how much is produced.

Let us consider a more complicated example. A recipe for pancakes calls for 2 cups (c) of pancake mix, 1 egg, and 1/2 c of milk. We can write this in the form of a chemical equation:

2 c mix + 1 egg + 1/2 c milk → 1 batch of pancakes

If you have 9 c of pancake mix, how many eggs and how much milk do you need? It might take a little bit of work, but eventually you will find you need 4½ eggs and 2¼ c milk.

How can we formalize this? We can make a conversion factor using our original recipe and use that conversion factor to convert from a quantity of one substance to a quantity of another substance. This is similar to the way we constructed a conversion factor between feet and yards in Chapter 2. Because one recipe's worth of pancakes requires 2 c of pancake mix, 1 egg, and 1/2 c of milk, we actually have the following mathematical relationships that relate these quantities:

2 c pancake mix ⇔ 1 egg ⇔ 1/2 c milk

where ⇔ is the mathematical symbol for "is equivalent to." This does not mean that 2 c of pancake mix equal 1 egg. However, *as far as this recipe is concerned*, these are the equivalent quantities needed for a single recipe of pancakes. So, any possible quantities of two or more ingredients must have the same numerical ratio as the ratios in the equivalence.

We can deal with these equivalences in the same way we deal with equalities in unit conversions: we can make conversion factors that essentially equal 1. For example, to determine how many eggs we need for 9 c of pancake mix, we construct the conversion factor:

$$\frac{1\,egg}{2\,c\,pancake\,mix}$$

This conversion factor is, in a strange way, equivalent to 1 because the recipe relates the two quantities. Starting with our initial quantity and multiplying by our conversion factor,

$$9\,\cancel{c\,pancake\,mix} \times \frac{1\,egg}{2\,\cancel{c\,pancake\,mix}} = 4.5\,eggs$$

Note how the units *cups pancake mix* canceled, leaving us with units of *eggs*. This is the formal, mathematical way of getting our amounts to mix with 9 c of pancake mix. We can use a similar conversion factor for the amount of milk:

$$9\,\cancel{c\,pancake\,mix} \times \frac{\frac{1}{2}\,c\,milk}{2\,\cancel{c\,pancake\,mix}} = 2.25\,c\,milk$$

Again, units cancel, and new units are introduced.

A balanced chemical equation is nothing more than *a recipe for a chemical reaction*. The difference is that a balanced chemical equation is written in terms of atoms and molecules, not cups, pounds, and eggs.

For example, consider the following chemical equation:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

We can interpret this as, literally, "two hydrogen molecules react with one oxygen molecule to make two water molecules." That interpretation leads us directly to some equivalencies, just as our pancake recipe did:

$$2H_2 \text{ molecules} \Leftrightarrow 1O_2 \text{ molecule} \Leftrightarrow 2H_2O \text{ molecules}$$

These equivalences allow us to construct conversion factors:

$$\frac{2\,molecules\,H_2}{1\,molecule\,O_2} \quad \frac{2\,molecules\,H_2}{2\,molecules\,H_2O} \quad \frac{1\,molecule\,H_2}{2\,molecules\,H_2O}$$

and so forth. These conversions can be used to relate quantities of one substance to quantities of another. For example, suppose we need to know how many molecules of oxygen are needed to react with 16 molecules of H_2. As we did with converting units, we start with our given quantity and use the appropriate conversion factor:

$$\cancel{16\,molecules\,H_2} \times \frac{1\,molecules\,O_2}{\cancel{2\,molecules\,H_2}} = 8\,molecules\,O_2$$

Note how the unit *molecules* H_2 cancels algebraically, just as any unit does in a conversion like this. The conversion factor came directly from the coefficients in the balanced chemical equation. This is another reason why a properly balanced chemical equation is important.

Example 11.6.1

How many molecules of SO_3 are needed to react with 144 molecules of Fe_2O_3 given this balanced chemical equation?

$$Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$$

Solution

We use the balanced chemical equation to construct a conversion factor between Fe_2O_3 and SO_3. The number of molecules of Fe_2O_3 goes on the bottom of our conversion factor so it cancels with our given amount, and the molecules of SO_3 go on the top. Thus, the appropriate conversion factor is

$$\frac{3\,molecules\,SO_3}{1\,molecule\,Fe_2O_3}$$

Starting with our given amount and applying the conversion factor, the result is

$$144\ \cancel{molecules}\ Fe_2O_3 \times \frac{3\,molecules\,SO_3}{1\ \cancel{molecule}\ Fe_2O_3} = 432\,molecules\,SO_3$$

We need 432 molecules of SO_3 to react with 144 molecules of Fe_2O_3.

Exercise 11.6.1

How many molecules of H_2 are needed to react with 29 molecules of N_2 to make ammonia if the balanced chemical equation is:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3?$$

Answer

87 molecules

Chemical equations also allow us to make conversions regarding the number of atoms in a chemical reaction, because a chemical formula lists the number of atoms of each element in a compound. The formula H_2O indicates that there are two hydrogen atoms and one oxygen atom in each molecule, and these relationships can be used to make conversion factors:

$$\frac{2\,atoms\,H}{1\,molecule\,H_2O} \quad \frac{1\,molecule\,H_2O}{1\,atom\,O}$$

Conversion factors like this can also be used in stoichiometry calculations.

Example 11.6.2

How many molecules of NH_3 can you make if you have 228 atoms of H_2?

Solution

From the formula, we know that one molecule of NH_3 has three H atoms. Use that fact as a conversion factor:

$$228\ \cancel{atoms\,H} \times \frac{1\,molecule\,NH_3}{3\ \cancel{atoms\,H}} = 76\,NH_3$$

Exercise 11.6.2

How many molecules of $Fe_2(SO_4)_3$ can you make from 777 atoms of S?

Answer

259 molecules

Summary

Quantities of substances can be related to each other using balanced chemical equations.

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11.7: The Mole

Learning Objectives

- Describe the unit *mole*.
- Relate the mole quantity of substance to its mass.

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances an atom or a molecule at a time; we work with millions, billions, and trillions of atoms and molecules at a time. We need a way to deal with macroscopic, rather than microscopic, amounts of matter. We need a unit of amount that relates quantities of substances on a scale that we can interact with.

Chemistry uses a unit called mole. A **mole** (mol) is a number of things equal to the number of atoms in exactly 12 g of carbon-12. Experimental measurements have determined that this number is very large:

$$1 \text{ mol} = 6.02214179 \times 10^{23} \text{ things}$$

Understand that a mole means a specific number of things, just like a dozen means a certain number of things—twelve, in the case of a dozen. But a mole is a much larger number of things. These things can be atoms, or molecules, or eggs; however, in chemistry, we usually use the mole to refer to the amounts of atoms or molecules. Although the number of things in a mole is known to eight decimal places, it is usually fine to use only two or three decimal places in calculations. The numerical value of things in a mole is often called *Avogadro's number* (N_A). *Avogadro's number* is also known as the *Avogadro constant*, after Amadeo Avogadro, an Italian chemist who first proposed its importance.

Example 11.7.1

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Also, because we know that there are three atoms in each molecule of H_2O, we can also determine the number of atoms in the sample.

$$2.76 \ \cancel{mol\ H_2O} \times \frac{6.022 \times 10^{23} molecules\ H_2O}{\cancel{mol\ H_2O}} = 1.66 \times 10^{24} molecules\ H_2O$$

To determine the total number of atoms, we have

$$1.66 \times 10^{24} \ \cancel{molecules\ H_2O} \times \frac{3\ atoms}{1\ molecule} = 4.99 \times 10^{24}\ atoms$$

Exercise 11.7.1

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

How big is a mole? It is very large. Suppose you had a mole of dollar bills that need to be counted. If everyone on earth (about 6 billion people) counted one bill per second, it would take about 3.2 million years to count all the bills. A mole of sand would fill a cube about 32 km on a side. A mole of pennies stacked on top of each other would have about the same diameter as our galaxy, the Milky Way. A mole is a lot of things—but atoms and molecules are very tiny. One mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket.

Why is the mole unit so important? It represents the link between the microscopic and the macroscopic, especially in terms of mass. *A mole of a substance has the same mass in grams as one unit (atom or molecules) has in atomic mass units*. The mole unit

allows us to express amounts of atoms and molecules in visible amounts that we can understand.

For example, we already know that, by definition, a mole of carbon has a mass of exactly 12 g. This means that exactly 12 g of C has 6.022×10^{23} atoms:

$$12 \text{ g C} = 6.022 \times 10^{23} \text{ atoms C}$$

We can use this equality as a conversion factor between the number of atoms of carbon and the number of grams of carbon. How many grams are there, say, in 1.50×10^{25} atoms of carbon? This is a one-step conversion:

$$1.50 \times 10^{25} \cancel{\text{ atoms C}} \times \frac{12.0000\, g\, C}{6.022 \times 10^{23} \cancel{\text{ atoms C}}} = 299\, g\, C$$

But it also goes beyond carbon. Previously we defined atomic and molecular masses as the number of atomic mass units per atom or molecule. Now we can do so in terms of grams. The atomic mass of an element is the number of grams in 1 mol of atoms of that element, while the molecular mass of a compound is the number of grams in 1 mol of molecules of that compound. Sometimes these masses are called **molar masses** to emphasize the fact that they are the mass for 1 mol of things. (The term *molar* is the adjective form of mole and has nothing to do with teeth.)

Here are some examples. The mass of a hydrogen atom is 1.0079 u; the mass of 1 mol of hydrogen atoms is 1.0079 g. Elemental hydrogen exists as a diatomic molecule, H_2. One molecule has a mass of 1.0079 + 1.0079 = 2.0158 u, while 1 mol H_2 has a mass of 2.0158 g. A molecule of H_2O has a mass of about 18.01 u; 1 mol H_2O has a mass of 18.01 g. A single unit of NaCl has a mass of 58.45 u; NaCl has a molar mass of 58.45 g. In each of these moles of substances, there are 6.022×10^{23} units: 6.022×10^{23} atoms of H, 6.022×10^{23} molecules of H_2 and H_2O, 6.022×10^{23} units of NaCl ions. These relationships give us plenty of opportunities to construct conversion factors for simple calculations.

Example 11.7.2: Sugar

What is the molar mass of sugar ($C_6H_{12}O_6$)?

Solution

To determine the molar mass, we simply add the atomic masses of the atoms in the molecular formula; but express the total in grams per mole, not atomic mass units. The masses of the atoms can be taken from the periodic table.

Solutions to Example 5.3.2

6 C = 6 × 12.011	= 72.066
12 H = 12 × 1.0079	= 12.0948
6 O = 6 × 15.999	= 95.994
TOTAL	= 180.155 g/mol

Per convention, the unit *grams per mole* is written as a fraction.

Exercise 11.7.2

What is the molar mass of $AgNO_3$?

Answer

169.87 g/mol

Knowing the molar mass of a substance, we can calculate the number of moles in a certain mass of a substance and vice versa, as these examples illustrate. The molar mass is used as the conversion factor.

Example 11.7.3

What is the mass of 3.56 mol of $HgCl_2$? The molar mass of $HgCl_2$ is 271.49 g/mol.

Solution

Use the molar mass as a conversion factor between moles and grams. Because we want to cancel the mole unit and introduce the gram unit, we can use the molar mass as given:

$$3.56 \cancel{mol\ HgCl_2} \times \frac{271.49\ g\ HgCl_2}{\cancel{mol\ HgCl_2}} = 967\ g\ HgCl_2$$

Exercise 11.7.3

What is the mass of 33.7 mol of H_2O?

Answer

607 g

Example 11.7.4

How many moles of H_2O are present in 240.0 g of water (about the mass of a cup of water)?

Solution

Use the molar mass of H_2O as a conversion factor from mass to moles. The molar mass of water is

$$(1.0079 + 1.0079 + 15.999) = 18.015\ g/mol.$$

However, because we want to cancel the gram unit and introduce moles, we need to take the reciprocal of this quantity, or 1 mol/18.015 g:

$$240.0\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}} = 13.32\ mol\ H_2O$$

Exercise 11.7.4

How many moles are present in 35.6 g of H_2SO_4 (molar mass = 98.08 g/mol)?

Answer

0.363 mol

Other conversion factors can be combined with the definition of mole—density, for example.

Example 11.7.5

The density of ethanol is 0.789 g/mL. How many moles are in 100.0 mL of ethanol? The molar mass of ethanol is 46.08 g/mol.

Solution

Here, we use density to convert from volume to mass and then use the molar mass to determine the number of moles.

$$100\ \cancel{ml}\ ethanol \times \frac{0.789\ g}{\cancel{ml}} \times \frac{1\ mol}{46.08\ \cancel{g}} = 1.71\ mol\ ethanol$$

Exercise 11.7.5

If the density of benzene, C_6H_6, is 0.879 g/mL, how many moles are present in 17.9 mL of benzene?

Answer

0.201 mol

Summary

The mole is a key unit in chemistry. The molar mass of a substance, in grams, is numerically equal to one atom's or molecule's mass in atomic mass units.

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11.7.1: The Mole in Chemical Reactions

Learning Objectives

- Balance a chemical equation in terms of moles.
- Use the balanced equation to construct conversion factors in terms of moles.
- Calculate moles of one substance from moles of another substance using a balanced chemical equation.

Consider this balanced chemical equation:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

We interpret this as "two molecules of hydrogen react with one molecule of oxygen to make two molecules of water." The chemical equation is balanced as long as the coefficients are in the ratio 2:1:2. For instance, this chemical equation is also balanced:

$$100\,H_2 + 50\,O_2 \longrightarrow 100\,H_2O$$

This equation is not conventional—because convention says that we use the lowest ratio of coefficients—but it is balanced. So is this chemical equation:

$$5{,}000\,H_2 + 2{,}500\,O_2 \longrightarrow 5{,}000\,H_2O$$

Again, this is not conventional, but it is still balanced. Suppose we use a much larger number:

$$12.044 \times 10^{23} H_2 + 6.022 \times 10^{23} O_2 \rightarrow 12.044 \times 10^{23} H_2O$$

These coefficients are also in the ratio of 2:1:2. But these numbers are related to the number of things in a mole: the first and last numbers are two times Avogadro's number, while the second number is Avogadro's number. That means that the first and last numbers represent 2 mol, while the middle number is just 1 mol. Well, why not just use the number of moles in balancing the chemical equation?

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

is the same balanced chemical equation we started with! What this means is that chemical equations are not just balanced in terms of molecules; *they are also balanced in terms of moles*. We can just as easily read this chemical equation as "two moles of hydrogen react with one mole of oxygen to make two moles of water." All balanced chemical reactions are balanced in terms of moles.

Example 11.7.1.1

Interpret this balanced chemical equation in terms of moles.

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10}$$

Solution

The coefficients represent the number of moles that react, not just molecules. We would speak of this equation as "one mole of molecular phosphorus reacts with five moles of elemental oxygen to make one mole of tetraphosphorus decoxide."

Exercise 11.7.1.1

Interpret this balanced chemical equation in terms of moles.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

Answer

One mole of elemental nitrogen reacts with three moles of elemental hydrogen to produce two moles of ammonia.

In Section 4.1, we stated that a chemical equation is simply a recipe for a chemical reaction. As such, chemical equations also give us equivalents—equivalents between the reactants and the products. However, now we understand that *these equivalents are expressed in terms of moles*. Consider the chemical equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

This chemical reaction gives us the following equivalents:

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$

Any two of these quantities can be used to construct a conversion factor that lets us relate the number of moles of one substance to an equivalent number of moles of another substance. If, for example, we want to know how many moles of oxygen will react with 17.6 mol of hydrogen, we construct a conversion factor between 2 mol of H_2 and 1 mol of O_2 and use it to convert from moles of one substance to moles of another:

$$17.6\,\cancel{mol\,H_2} \times \frac{1\,mol\,O_2}{2\,\cancel{mol\,H_2}} = 8.80\,mol\,O_2$$

Note how the mol H_2 unit cancels, and mol O_2 is the new unit introduced. This is an example of a **mole-mole calculation,** when you start with moles of one substance and convert to moles of another substance by using the balanced chemical equation. The example may seem simple because the numbers are small, but numbers won't always be so simple!

Example 11.7.1.2

For the balanced chemical equation

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

if 154 mol of O_2 are reacted, how many moles of CO_2 are produced?

Solution

We are relating an amount of oxygen to an amount of carbon dioxide, so we need the equivalence between these two substances. According to the balanced chemical equation, the equivalence is

$$13 \text{ mol } O_2 \Leftrightarrow 8 \text{ mol } CO_2$$

We can use this equivalence to construct the proper conversion factor. We start with what we are given and apply the conversion factor:

$$154\,\cancel{mol\,O_2} \times \frac{8\,mol\,CO_2}{13\,\cancel{mol\,O_2}} = 94.8\,mol\,CO_2$$

The mol O_2 unit is in the denominator of the conversion factor so it cancels. Both the 8 and the 13 are exact numbers, so they do not contribute to the number of significant figures in the final answer.

Exercise 11.7.1.2

Using the above equation, how many moles of H_2O are produced when 154 mol of O_2 react?

Answer

118 mol

It is important to reiterate that balanced chemical equations are balanced in terms of *moles*. Not grams, kilograms, or liters—but moles. Any stoichiometry problem will likely need to work through the mole unit at some point, especially if you are working with a balanced chemical reaction.

Summary

Balanced chemical reactions are balanced in terms of moles. A balanced chemical reaction gives equivalents in moles that allow stoichiometry calculations to be performed.

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