CHEM 1000 - INTRODUCTION TO CHEMISTRY (RIVERLAND)



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Licensing

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CHAPTER OVERVIEW

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1.1: The Scope of 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.

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

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

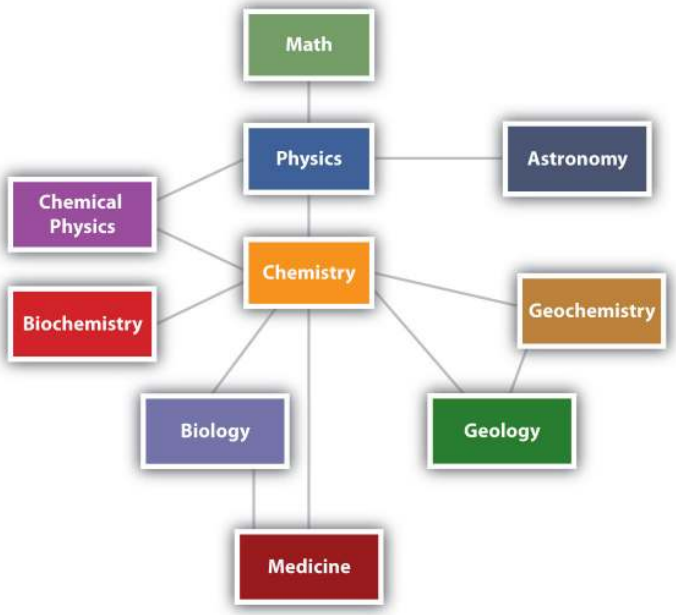


Figure **1.1.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure **1.1.1** shows how many of the individual fields of science are related. At some level, all of these fields depend on matter because they all involve "stuff"; because of this, chemistry has been called the "central science", linking them all together.

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

Example 1.1.1: Science Fields

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

Solution

a. Sculpture is not considered a science because it is not a study of some aspect of the natural universe.
b. Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

Exercise 1.1.1

Which fields of study are branches of science?

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

Answer a:

yes

Answer b:

yes

Answer c:

yes

Answer d:

no

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. 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, in general, are not primarily based on 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 anything from basic cellular processes up to understanding disease states so that better treatments can be developed.



Figure 1.1.2: (left) Measurement of trace metals using atomic spectroscopy. (right) Measurement of 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 bioinorganic chemistry or physical organic chemistry.

History of Chemistry

The **history** of chemistry is an interesting and challenging one. Very early chemists were often motivated mainly by the achievement of a specific goal or product. Making perfume or soaps did not need a lot of **theory**, just a good recipe and careful attention to detail. There was no standard way of naming materials (and no periodic table that we could all agree on). It is often difficult to figure out exactly what a particular person was using. However, the science developed over the centuries by trial and error.

Major progress was made toward putting chemistry on a solid foundation when Robert Boyle (1637-1691) began his **research** in chemistry (Figure 1.1.3). He developed the basic ideas about the behavior of gases. He could then describe gases mathematically. Boyle also helped form the idea that small particles could combine to form molecules. Many years later, John Dalton used these ideas to develop the atomic theory.



Figure 1.1.3: Robert Boyle.

The field of chemistry began to develop rapidly in the 1700's. Joseph Priestley (1733-1804) isolated and characterized several gases: oxygen, carbon monoxide, and nitrous oxide. It was later discovered that nitrous oxide ("laughing gas") worked as an anesthetic. This gas was used for that purpose for the first time in 1844 during a tooth extraction. Other gases discovered during that time were chlorine, by C.W. Scheele (1742-1786) and nitrogen, by Antoine Lavoisier (1743-1794). Lavoisier has been considered by many scholars to be the "father of chemistry". Among other accomplishments, he discovered the role of oxygen in combustion and definitively formulated the law of conservation of matter.

Chemists continued to discover new compounds in the 1800's. The science also began to develop a more theoretical foundation. John Dalton (1766-1844) put forth his atomic theory in 1807. This idea allowed scientists to think about chemistry in a much more systematic way. Amadeo Avogadro (1776-1856) laid the groundwork for a more quantitative approach to chemistry by calculating the number of particles in a given amount of a gas. A lot of effort was put forth in studying chemical reactions. These efforts led to new materials being produced. Following the invention of the battery by Alessandro Volta (1745-1827), the field of electrochemistry (both theoretical and applications) developed through major contributions by Humphry Davy (1778-1829) and Michael Faraday (1791-1867). Other areas of the discipline also progressed rapidly.

It would take a large book to cover developments in chemistry during the twentieth century and up to today. One major area of expansion was in the area of the chemistry of living processes. Research in photosynthesis in plants, the discovery and

characterization of enzymes as biochemical catalysts, elucidation of the structures of biomolecules such as insulin and DNA—these efforts gave rise to an explosion of information in the field of biochemistry.

The practical aspects of chemistry were not ignored. The work of Volta, Davy, and Faraday eventually led to the development of batteries that provided a source of electricity to power a number of devices (Figure **1.1.4**).

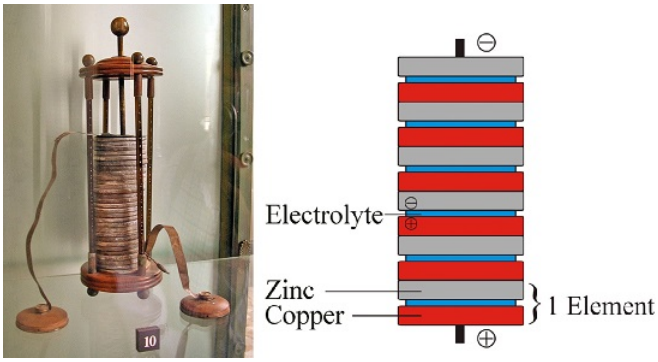


Figure **1.1.4**: Battery developed by Volta. (CC BY-SA 3.0; (left) GuidoB and (right) Kkkdc).

Charles Goodyear (1800-1860) discovered the process of vulcanization, allowing a stable rubber product to be produced for the tires of all the vehicles we have today. Louis Pasteur (1822-1895) pioneered the use of heat sterilization to eliminate unwanted microorganisms in wine and milk. Alfred Nobel (1833-1896) invented dynamite (Figure **1.1.5**). After his death, the fortune he made from this product was used to fund the Nobel Prizes in science and the humanities. J.W. Hyatt (1837-1920) developed the first plastic. Leo Baekeland (1863-1944) developed the first synthetic resin, widely used for inexpensive and sturdy dinnerware.



Figure **1.1.5**: Dynamite explosion in Panama, Central America (1908).

Today, chemistry continues to be essential to the development of new materials and technologies, from semiconductors for electronics to powerful new medicines, and beyond.

Summary

- Chemistry is the study of matter and the changes it undergoes and considers both *macroscopic* and *microscopic* information.
- Matter is anything that has mass and occupies space.
- The five main disciplines of chemistry are physical chemistry, organic chemistry, inorganic chemistry, analytical chemistry and biochemistry.
- Many civilizations contributed to the growth of chemistry. A lot of early chemical research focused on practical uses. Basic chemistry theories were developed during the nineteenth century. New materials and batteries are a few of the products of modern chemistry.

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1.2: Chemicals Compose Ordinary Things

Chemistry is the branch of science dealing with the structure, composition, properties, and the reactive characteristics of matter. Matter is anything that has mass and occupies space. Thus, chemistry is the study of literally everything around us—the liquids that we drink, the gases we breathe, the composition of everything from the plastic case on your phone to the earth beneath your feet. Moreover, chemistry is the study of the transformation of matter. Crude oil is transformed into more useful petroleum products, such as gasoline and kerosene, by the process of refining. Some of these products are further transformed into plastics. Crude metal ores are transformed into metals, that can then be fashioned into everything from foil to automobiles. Potential drugs are identified from natural sources, isolated and then prepared in the laboratory. Their structures are systematically modified to produce the pharmaceuticals that have led to vast advances in modern medicine. Chemistry is at the center of all of these processes; chemists are the people that study the nature of matter and learn to design, predict, and control these chemical transformations. Within the branches of chemistry you will find several apparent subdivisions. Inorganic chemistry, historically, focused on minerals and metals found in the earth, while organic chemistry dealt with carbon-containing compounds that were first identified in living things. Biochemistry is an outgrowth of the application of organic chemistry to biology and relates to the chemical basis for living things. In the later chapters of this text we will explore organic and biochemistry in a bit more detail and you will notice examples of organic compounds scattered throughout the text. Today, the lines between the various fields have blurred significantly and a contemporary chemist is expected to have a broad background in all of these areas.

In this chapter, we will discuss some of the properties of matter and how chemists measure those properties. We will introduce some of the vocabulary that is used throughout chemistry and the other physical sciences.

Let's begin with matter. **Matter** is defined as any substance that has mass. It is important to distinguish here between weight and mass. Weight is the result of the pull of gravity on an object. On the Moon, an object will weigh less than the same object on Earth because the pull of gravity is less on the Moon. The mass of an object, however, is an inherent property of that object and does not change, regardless of location, gravitational pull, or anything else. It is a property that is solely dependent on the quantity of matter within the object.

Contemporary theories suggests that matter is composed of **atoms**. Atoms themselves are constructed from neutrons, protons and electrons, along with an ever-increasing array of other subatomic particles. We will focus on the neutron, a particle having no charge; the proton, which carries a positive charge; and the electron, which has a negative charge. Atoms are incredibly small. To give you an idea of the size of an atom, a single copper penny contains approximately 28,000,000,000,000,000,000,000 atoms (that's 28 sextillion). Because atoms and subatomic particles are so small, their mass is not readily measured using pounds, ounces, grams or any other scale that we would use on larger objects. Instead, the mass of atoms and subatomic particles is measured using atomic mass units (abbreviated amu). The atomic mass unit is based on a scale that relates the mass of different types of atoms to each other (using the most common form of the element carbon as a standard). The amu scale gives us a convenient means to describe the masses of individual atoms and to do quantitative measurements concerning atoms and their reactions. Within an atom, the neutron and proton both have a mass of one amu; the electron has a much smaller mass (about 0.0005 amu).



Figure **1.2.1**: Atoms are incredible small. To give you an idea of the size of an atom, a single copper penny contains approximately 28,000,000,000,000,000,000,000 atoms (that's 28 sextillion).

Atomic theory places the neutron and the proton in the center of the atom in the nucleus. In an atom, the nucleus is very small, very dense, carries a positive charge (from the protons) and contains virtually all of the mass of the atom. Electrons are placed in a diffuse cloud surrounding the nucleus. The electron cloud carries a net negative charge (from the charge on the electrons) and in a neutral atom there are always as many electrons in this cloud as there are protons in the nucleus (the positive charges in the nucleus are balanced by the negative charges of the electrons, making the atom neutral).

An atom is characterized by the number of neutrons, protons and electrons that it possesses. Today, we recognize at least 116 different types of atoms, each type having a different number of protons in its nucleus. These different types of atoms are called elements. The neutral element hydrogen (the lightest element) will always have one proton in its nucleus and one electron in the cloud surrounding the nucleus. The element helium will always have two protons in its nucleus. It is the number of protons in the nucleus of an atom that defines the identity of an element. Elements can, however, have differing numbers of neutrons in their nucleus. For example, stable helium nuclei exist that contain one, or two neutrons (but they all have two protons). These different types of helium atoms have different masses (3 or 4 amu) and they are called isotopes. For any given isotope, the sum of the numbers of protons and neutrons in the nucleus is called the mass number. All elements exist as a collection of isotopes, and the mass of an element that we use in chemistry, the atomic mass, is the average of the masses of these isotopes. For helium, there is approximately one isotope of Helium-3 for every one million isotopes of Helium-4, hence the average atomic mass is very close to 4 (4.002602).

As different elements were discovered and named, abbreviations of their names were developed to allow for a convenient chemical shorthand. The abbreviation for an element is called its chemical symbol. A chemical symbol consists of one or two letters, and the relationship between the symbol and the name of the element is generally apparent. Thus helium has the chemical symbol He, nitrogen is N, and lithium is Li. Sometimes the symbol is less apparent but is decipherable; magnesium is Mg, strontium is Sr, and manganese is Mn. Symbols for elements that have been known since ancient times, however, are often based on Latin or Greek names and appear somewhat obscure from their modern English names. For example, copper is Cu (from cuprum), silver is Ag (from argentum), gold is Au (from aurum), and iron is Fe (from ferrum). Throughout your study of chemistry, you will routinely use chemical symbols and it is important that you begin the process of learning the names and chemical symbols for the common elements. By the time you complete General Chemistry, you will find that you are adept at naming and identifying virtually all of the 116 known elements. Table **1.2.1** contains a starter list of common elements that you should begin learning now!

Table **1.2.1**: Names and Chemical Symbols for Common Elements

Element	Chemical Symbol	Element	Chemical Symbol
Hydrogen	H	Phosphorus	P
Helium	He	Sulfur	S
Lithium	Li	Chlorine	Cl
Beryllium	Be	Argon	Ar
Boron	B	Potassium	K
Carbon	C	Calcium	Ca
Nitrogen	N	Iron	Fe
Oxygen	O	Copper	Cu
Fluorine	F	Zinc	Zn
Neon	Ne	Bromine	Br
Sodium	Na	Silver	Ag
Magnesium	Mg	Iodine	I
Aluminum	Al	Gold	Au
Silicon	Si	Lead	Pb

The chemical symbol for an element is often combined with information regarding the number of protons and neutrons in a particular isotope of that atom to give the atomic symbol. To write an atomic symbol, begin with the chemical symbol, then write the atomic number for the element (the number of protons in the nucleus) as a subscript, preceding the chemical symbol. Directly above this, as a superscript, write the mass number for the isotope, that is, the total number of protons and neutrons in the nucleus.

Thus, for helium, the atomic number is 2 and there are two neutrons in the nucleus for the most common isotope, making the atomic symbol $^{4}_{2}\mathrm{He}$. In the definition of the atomic mass unit, the "most common isotope of carbon", $^{12}_{6}\mathrm{C}$, is defined as having a mass of exactly 12 amu and the atomic masses of the remaining elements are based on their masses relative to this isotope. Chlorine (chemical symbol Cl) consists of two major isotopes, one with 18 neutrons (the most common, comprising 75.77% of natural chlorine atoms) and one with 20 neutrons (the remaining 24.23%). The atomic number of chlorine is 17 (it has 17 protons in its nucleus), therefore the chemical symbols for the two isotopes are $^{35}_{17}\mathrm{Cl}$ and $^{37}_{17}\mathrm{Cl}$.

When data is available regarding the natural abundance of various isotopes of an element, it is simple to calculate the average atomic mass. In the example above, $^{35}_{17}\mathrm{Cl}$ was the most common isotope with an abundance of 75.77% and $^{37}_{17}\mathrm{Cl}$ had an abundance of the remaining 24.23%. To calculate the average mass, first convert the percentages into fractions; that is, simply divide them by 100. Now, chlorine-35 represents a fraction of natural chlorine of 0.7577 and has a mass of 35 (the mass number). Multiplying these, we get (0.7577 × 35) = 26.51. To this, we need to add the fraction representing chlorine-37, or (0.2423 × 37) = 8.965; adding, (26.51 + 8.965) = 35.48, which is the weighted average atomic mass for chlorine. Whenever we do mass calculations involving elements or compounds (combinations of elements), we always need to use average atomic masses.

Contributions & Attributions

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1.3: Hypothesis, Theories, and Laws

Learning Objectives

- Describe the difference between hypothesis and theory as scientific terms.
- Describe the difference between a theory and scientific law.

Although many have taken science classes throughout the course of their studies, people often have incorrect or misleading ideas about some of the most important and basic principles in science. Most students have heard of hypotheses, theories, and laws, but what do these terms really mean? Prior to reading this section, consider what you have learned about these terms before. What do these terms mean to you? What do you read that contradicts or supports what you thought?

What is a Fact?

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

What is a Hypothesis?

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

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

> *A hypothesis is very tentative; it can be easily changed.*

What is a Theory?

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

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

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

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

> *Theories aren't likely to change.*

What is a Law?

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

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

What is a Belief?

A **belief** is a statement that is not scientifically provable. Beliefs may or may not be incorrect; they just are outside the realm of science to explore.

Laws vs. Theories

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



Video **1.3.1**: What's the difference between a scientific law and theory?

Summary

- A hypothesis is a tentative explanation that can be tested by further investigation.
- A theory is a well-supported explanation of observations.
- A scientific law is a statement that summarizes the relationship between variables.
- An experiment is a controlled method of testing a hypothesis.

Contributions & Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
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1.4: The Scientific Method - How Chemists Think

Learning Objectives

- Identify the components of 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 leads to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.4.1).

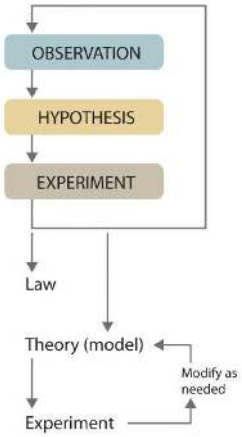


Figure 1.4.1: The Steps in the Scientific Method.

Step 1: Make observations

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

Step 2: Formulate a hypothesis

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

a. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun.
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 or not the original hypothesis is valid. If the hypothesis is valid, the scientist can proceed to step 5. In other cases, experiments often demonstrate that the hypothesis is incorrect or that it must be modified and requires further experimentation.

Step 5: Development into a law and/or theory

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

One example of a law, the law of definite proportions, 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 **1.4.1** at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

✔ Example 1.4.1

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

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

Solution

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

? Exercise 1.4.1

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 to ever play professional basketball.
e. Limestone is relatively insoluble in water, but dissolves readily in dilute acid with the evolution of a gas.

Answer a
experiment
Answer b
law
Answer c
theory
Answer d
hypothesis
Answer e
observation

Summary

The scientific method is a method of investigation involving experimentation and observation to acquire new knowledge, solve problems, and answer questions. The key steps in the scientific method include the following:

- Step 1: Make observations.
- Step 2: Formulate a hypothesis.
- Step 3: Test the hypothesis through experimentation.
- Step 4: Accept or modify the hypothesis.
- Step 5: Develop into a law and/or a theory.

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- Wikipedia

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1.5: A Beginning Chemist - How to Succeed

Examples of the practical applications of chemistry are everywhere (Figure **1.5.1**). Engineers need to understand the chemical properties of the substances needed to design biologically compatible implants for joint replacements; or to design roads, bridges, buildings, and nuclear reactors that do not collapse because of weakened structural materials such as steel and cement. Archeology and paleontology rely on chemical techniques to date bones and artifacts and identify their origins. Although law is not normally considered a field related to chemistry, forensic scientists use chemical methods to analyze blood, fibers, and other evidence as they investigate crimes. In particular, DNA matching—comparing biological samples of genetic material to see whether they could have come from the same person—has been used to solve many high-profile criminal cases as well as clear innocent people who have been wrongly accused or convicted. Forensics is a rapidly growing area of applied chemistry. In addition, the proliferation of chemical and biochemical innovations in industry is producing rapid growth in the area of patent law. Ultimately, the dispersal of information in all the fields in which chemistry plays a part requires experts who are able to explain complex chemical issues to the public through television, print journalism, the Internet, and popular books.

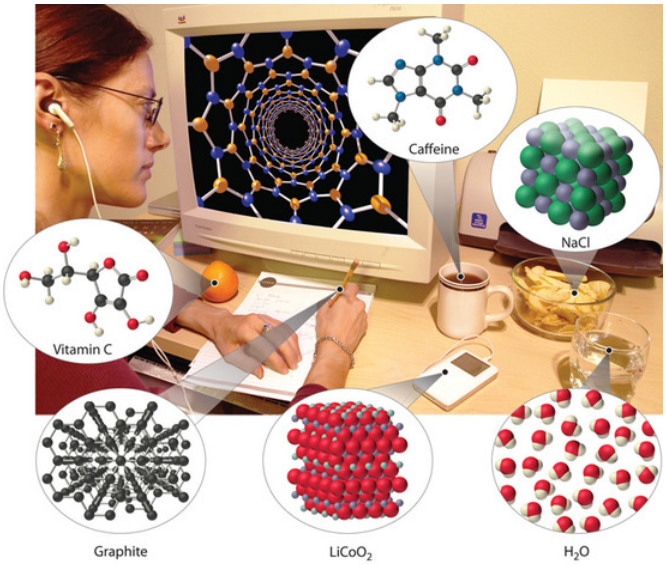


Figure **1.5.1**: Chemistry in Everyday Life. Although most people do not recognize it, chemistry and chemical compounds are crucial ingredients in almost everything we eat, wear, and use.

Chemical compounds in everyday life: Vitamin C, graphite, lithium cobalt oxide, caffeine, sodium chloride, water

Hopefully at this point you are fully convinced of how important and useful the study of chemistry can be. You may, however, still be wondering exactly *what* it is that a chemist does. Chemistry is the study of matter and the changes that matter undergoes. In general, chemists are interested in both characteristics that you can test and observe, like a chemical's smell or color, and characteristics that are far too small to see, like what the oxygen you breathe in or the carbon dioxide you breath out looks like under a microscope 1,000 times more powerful than any existing in the world today.

Wait a minute… how can a chemist *know* what oxygen and carbon dioxide look like under a microscope that doesn't even exist? What happened to the scientific method? What happened to relying on *observations* and *careful measurements*? In fact, because chemists *can't* see the underlying structure of different materials, they have to rely on the scientific method even more! Chemists are a lot like detectives. Suppose a detective is trying to solve a murder case—what do they do? Obviously, the detective starts by visiting the site of the crime and looking for evidence. If the murderer has left enough clues behind, the detective can piece together a theory explaining what happened.

Even though the detective wasn't at the crime scene when the crime was committed and didn't actually see the murderer kill the victim, with the right evidence, the detective can be pretty sure of how the crime took place. It is the same with chemistry. When chemists go into the laboratory, they collect evidence by making measurements. Once chemists have collected enough clues from the properties that they can observe, they use that evidence to piece together a theory explaining the properties that they cannot observe—the properties that are too small to see.

What kinds of properties do chemists actually measure in the laboratory? Well, you can probably guess a few. Imagine that you go to dinner at a friend's house and are served something that you don't recognize, what types of observations might you make to determine exactly *what* you've been given? You might smell the food. You might note the color of the food. You might try to decide whether the food is a liquid or a solid because if it's a liquid, it's probably soup or a drink. The temperature of the food could be useful if you wanted to know whether or not you had been served ice cream! You could also pick up a small amount of food with your fork and try to figure out how much it weighs—a light dessert might be something like an angel cake, while a heavy dessert is probably a pound cake. The quantity of food you have been given might be a clue too. Finally, you might want to know something about the food's texture—is it hard and granular like sugar cubes, or soft and easy to spread, like butter?

Believe it or not, the observations you are likely to make when trying to identify an unknown food are very similar to the observations that a chemist makes when trying to learn about a new material. Chemists rely on smell, color, state (whether it is a solid or liquid or gas), temperature, volume, mass (which is related to weight—as will be discussed in a later section), and texture. There is, however, one property possibly used to learn about a food, but that should *definitely* not be used to learn about a chemical—taste!

In the sections on the Atomic Theory, you will see exactly how measurements of certain properties helped early scientists to develop theories about the chemical structure of matter on a scale much smaller than they could ever hope to see. You will also learn how these theories, in turn, allow us to make predictions about new materials that humankind has not yet created.

The video below gives you some important tips on how to study chemistry in this class. With practice, you too can learn to think like a chemist, and you may even enjoy it!



Video **1.5.1**: How To Study Chemistry.

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1.6: Solving Society's Problems - Scientific Research

Learning Objective

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

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

Types of Research

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

Examples of "Pure" Research

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



Figure **1.6.1** *Ancient Greek philosophers.*

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

Examples of "Applied" Research

There is a great deal of "applied" research taking place today. In general, no new science principles are discovered, but existing knowledge is used to develop new products. Research on laundry detergents will probably not offer any new concepts of soap, but will help us develop materials that get our clothes cleaner, use less water, and create lower amounts of pollution.

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



Figure **1.6.2** A *Gasoline pump.*

Some "In-Between" Examples

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

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

Summary

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

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1.7: Cosmetics - Personal Care Chemicals

Learning Objectives

- List the main ingredients in different personal care products and their functions.
- Describe the steps in formation of temporary and permanent waves.

In the United States, the Food and Drug Administration (FDA), which regulates cosmetics, defines cosmetics as products "intended to be applied to the human body for cleansing, beautifying, promoting attractiveness, or altering the appearance without affecting the body's structure or functions". This broad definition includes any material intended for use as an ingredient of a cosmetic product, with the FDA specifically excluding pure soap from this category.



Figure **1.7.1** Assorted cosmetics and tools.

Cosmetics (Figure **1.7.1**) have been in use for thousands of years. Egyptian men and women used makeup to enhance their appearance. They were very fond of eyeliner and eye-shadows in dark colors including blue, red, and black. Ancient Sumerian men and women were possibly the first to invent and wear lipstick, about 5,000 years ago. They crushed gemstones and used them to decorate their faces, mainly on the lips and around the eyes.

According to one source, early major developments include:

- Kohl used by ancient Egypt as a protectant of the eye (Figure **1.7.2**).
- Castor oil used by ancient Egypt as a protective balm.
- Skin creams made of beeswax, olive oil, and rose water, described by Romans.
- Vaseline and lanolin in the nineteenth century.

Although modern makeup has been traditionally used mainly by women, an increasing number of men are using cosmetics usually associated with women to enhance or cover their own facial features such as blemishes and dark circles, as well the use of eyeshadow, mascara and lipstick by some. Cosmetics brands have increasingly also targeted men in the sale of cosmetics, with some products targeted specifically at men.

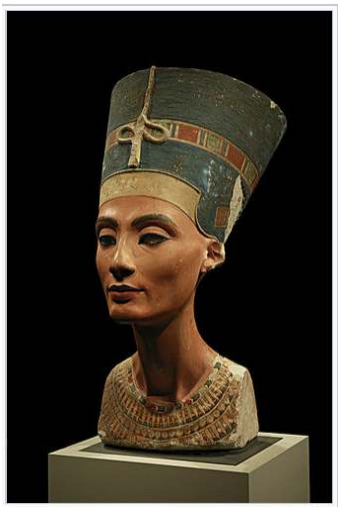


Figure **1.7.2** Nefertiti Bust showing the use of eye liner made of kohl.

The Skin

The cutaneous membrane is the technical term for our skin. The skin's primary role is to help protect the rest of the body's tissues and organs from physical damage such as abrasions, chemical damage such as detergents, and biological damage from microorganisms. For example, while the skin harbors many permanent and transient bacteria, these bacteria are unable to enter the body when healthy, intact skin is present.

Our skin is made of three general layers (Figure **1.7.3**). In order from most superficial to deepest they are the epidermis, dermis, and subcutaneous tissue (hypodermis).

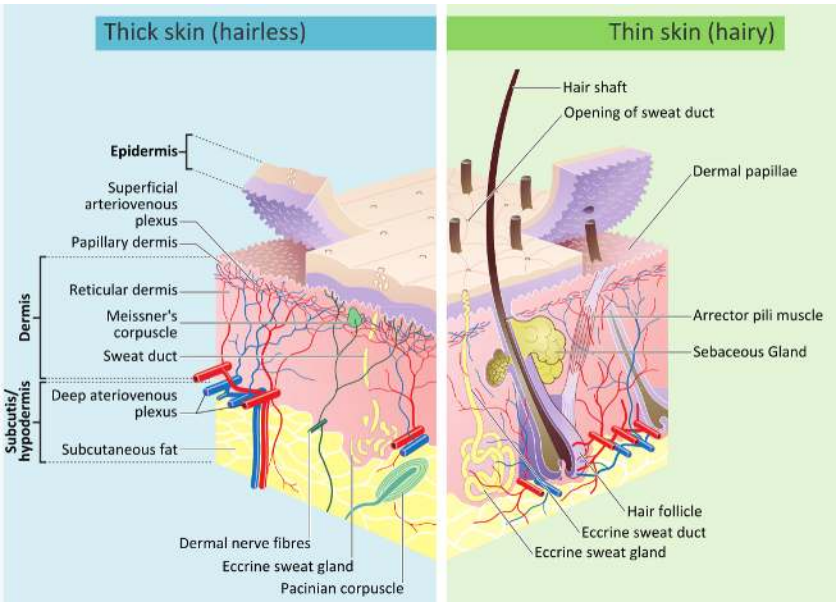


Figure **1.7.3** Skin layers, of both the hairy and hairless skin.

There are several different types of cells in the **epidermis**. All of the cells are necessary for the important functions of the epidermis.

- The epidermis consists mainly of stacks of keratin-producing epithelial cells called keratinocytes. These cells make up at least 90 percent of the epidermis. Near the top of the epidermis, these cells are also called squamous cells.
- Another 8 percent of epidermal cells are melanocytes. These cells produce the pigment melanin that protects the dermis from UV light.

- About 1 percent of epidermal cells are Langerhans cells. These are immune system cells that detect and fight pathogens entering the skin.
- Less than 1 percent of epidermal cells are Merkel cells, which respond to light touch and connect to nerve endings in the dermis.

The epidermis has several crucial functions in the body. These functions include protection, water retention, and vitamin D synthesis. The epidermis provides protection to underlying tissues from physical damage, pathogens, and UV light.

Skin Creams and Lotions

A **lotion** is a low-viscosity topical preparation intended for application to the skin. By contrast, creams and gels have higher viscosity, typically due to lower water content. Lotions are applied to external skin with bare hands, a brush, a clean cloth, or cotton wool.

While a lotion may be used as a medicine delivery system, many lotions, especially **hand lotions** and **body lotions** are meant instead to simply smooth, moisturize, soften and perhaps perfume the skin.

Most cosmetic lotions are moisturizing lotions, although other forms, such as tanning lotion, also exist.

Cosmetic lotions may be marketed as anti-aging lotions, which can also be classified as a cosmetic in many cases, and may contain fragrances. The Food and Drug Administration voiced concern about lotions not classified as drugs that advertise anti-aging or anti-wrinkle properties.

Most lotions are oil-in-water emulsions using a substance such as cetearyl alcohol to keep the emulsion together, but water-in-oil lotions are also formulated.

A **cream** is a preparation usually for application to the skin. Creams for application to mucous membranes such as those of the rectum or vagina are also used. Creams may be considered pharmaceutical products as even cosmetic creams are based on techniques developed by pharmacy and unmedicated creams are highly used in a variety of skin conditions (dermatoses). The use of the finger tip unit concept may be helpful in guiding how much topical cream is required to cover different areas.

Creams are semi-solid emulsions of oil and water. They are divided into two types: oil-in-water (O/W) creams which are composed of small droplets of oil dispersed in a continuous water phase, and water-in-oil (W/O) creams which are composed of small droplets of water dispersed in a continuous oily phase. Oil-in-water creams are more comfortable and cosmetically acceptable as they are less greasy and more easily washed off using water. Water-in-oil creams are more difficult to handle but many drugs which are incorporated into creams are hydrophobic and will be released more readily from a water-in-oil cream than an oil-in-water cream. Water-in-oil creams are also more moisturizing as they provide an oily barrier which reduces water loss from the stratum corneum, the outermost layer of the skin.

Ointment is a semisolid dosage form it is used for topical application to the medication

Water, oil, emulsifier, and thickening agent are four main ingredients of cold creams and lotions.

Moisturizer or **moisturiser** is a cosmetic preparation used for protecting, moisturizing, and lubricating the skin. These functions are normally performed by sebum produced by healthy skin.

Moisturizers modify the rate of water loss, with active ingredients of moisturizers falling into one of two categories: occlusives and humectants

Occlusives form a coating on the surface of the skin, keeping moisture from escaping.

Humectants absorb water. They can absorb this water from the air and moisturize the skin when the humidity is greater than 70%, but more commonly they draw water from the dermis into the epidermis, making skin dryer. A study published in Skin Research and Technology in 2001 found no link between humectants and moisturizing effect. When used in practical applications, they are almost always combined with occlusives.

Moisturizers often contain water, which acts as a temporary hydration agent and as a way for the absorption of some components and evaporation of the moisturizer.

There are many different types of moisturizers. Petrolatum is one of the most effective moisturizers, although it can be unpopular due to its oily consistency. Other popular moisturizers are cetyl alcohol, cetearyl alcohol, cocoa butter, isopropyl myristate, isopropyl palmitate, lanolin, liquid paraffin, polyethylene glycols, shea butter, silicone oils, stearic acid, stearyl alcohol and castor oil, as well as other oils.

Moisturizers may also be available as lotions, creams, ointments, bath oils, or soap substitutes.

Mineral oils and waxes are insensitive to oxidation or rancidity. For this reason, they have essentially replaced vegetable oils in emollients and topical medication.

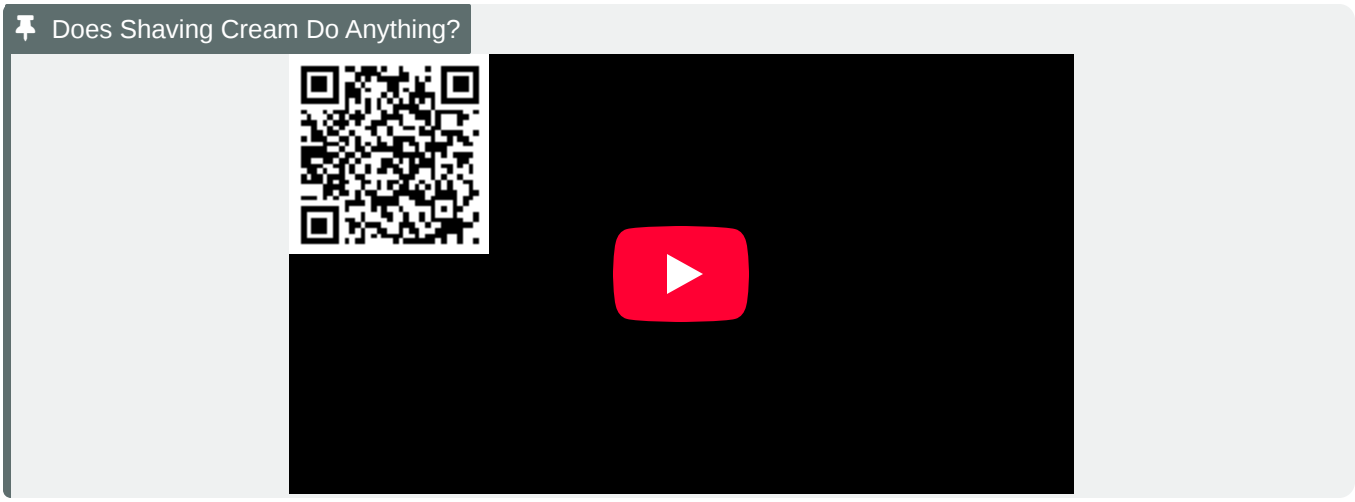
Moisturizer cosmetics may additionally contain antioxidants, ceramides, emulsifiers, fragrances, penetration enhancers, preservatives, and solvents. Some products are marketed as having anti-wrinkle and skin enhancement effects. Many plant and animal extracts have been claimed to impart skin benefits, with little scientific evidence.

Shaving Creams

Shaving cream or **shave cream** is a category of cosmetics used for shaving preparation. The purpose of shaving cream is to soften the hair by providing lubrication.

Different types of shaving creams include aerosol shaving cream (also known as shaving foam), latherless shaving cream (also called brushless shaving cream and non-aerosol shaving cream), and lather shaving cream or lathering shaving cream. The term shaving cream can also refer to the lather produced with a shaving brush from shaving soap or a lather shaving cream.

Shaving creams commonly consist of an emulsion of oils, soaps or surfactants (e.g. triethanolamine steatrate), and water. In addition to soap, lather shaving creams include a humectant for softer consistency and keeping the lather moisturised. Brushless shaving creams, on the other hand, don't contain soap and so don't produce lather. They are an oil-in-water mixture to which humectants, wetting agents, and other ingredients are added. Aerosol shaving creams are basically lather shaving cream in liquid form with propellants, vegetable waxes, and various oils added.



***Video* 1.7.1** *What is shaving cream?*

Sunscreen and Sunblock

UVB radiation in sunlight allows the skin to produce vitamin D. This vitamin prevents bone disorders like rickets and osteoporosis (brittle bone disease). The American Academy of Dermatology suggests vitamin D be obtained through foods or nutritional supplements. Excessive exposure to UV can be damaging and the pigment **melanin**, deposited in cells at the base of the epidermis, helps to protect the underlying layers of the skin from this damage. Melanin also colors the skin and variations in the amount of melanin produces colors from pale yellow to black. The darker the skin tone, the more melanin one has, and the less likely skin cancer will occur.

Excess exposure to the sun can cause sunburn. This is common in humans, but light skinned animals like cats and pigs can also be sunburned, especially on the ears. Skin cancer can also result from excessive exposure to the sun. As holes in the ozone layer

increase exposure to the sun's UV rays, so too does the rate of skin cancer in humans and animals.

Sunscreens and sunblocks are designed to protect skin from ultraviolet rays. *Sunblocks* contain inorganic ingredients like zinc oxide or titanium dioxide. These chemicals act as UV filters by reflecting the sun's UV rays. Sunblocks can have grainy textures due to the inorganic components. The thick nature of a sunblock can make it difficult to spread evenly on the skin. *Sunscreens* contain organic compounds like oxybenzone, avobenzone, homosalate, and octinoxate (Figure **1.7.4**). By absorbing ultraviolet rays, these compounds decompose and give off heat. Sunscreens apply smoother than sunblocks. Often, manufacturers will combine sunscreen and sunblock ingredients to make their products.



Figure **1.7.4** Chemistry of Sunscreen.

Sun protection factor (SPF) measures a product's protection from UVB rays. SPF does not quantify protection from UVA radiation. The American Academy of Dermatology recommends you select a sunscreen or sunblock with a minimum SPF factor of 30. This SPF value means a lotion can filter out 97% of UVB rays. Moving to a SPF of 50 will only filter out 1 more percentage of UVB rays. Increasing a SPF factor past 30 really does very little in shielding skin from UVB radiation.

Products that protect skin from UVA must be labeled as being a broad spectrum. Sunblocks provide UVA and UVB protection, but sunscreens can vary on what they can screen. Every two hours, sunscreens/sunblocks should be reapplied to the skin. Sweating and swimming can remove sunscreen/sunblock products. No sun products are waterproof, but some are labeled as being water-resistant. Consumers are encouraged to reapply these products every two hours as well.

Sunscreen Label

***Figure* 1.7.5** *Sunscreen label. Source: Badger: Healthy Body Care*

Is Sunscreen Safe?

Check the link below on FAQs regarding sunscreen.

https://www.aad.org/public/everyday-care/sun-protection/sunscreen/understand-sunscreen-labels

Lipsticks and Lip Balms

Lipstick, lip gloss, lip liner, lip plumper, lip balm, lip stain, lip conditioner, lip primer, lip boosters, and lip butters: Lipsticks are intended to add color and texture to the lips and often come in a wide range of colors, as well as finishes such as matte, satin, gloss and lustre.

Lipstick contains wax, oils, antioxidants, and emollients. Wax provides the structure to the solid lipstick. Lipsticks may be made from several waxes such as beeswax, ozokerite and candelilla wax. Because of its high melting point, carnauba wax is a key ingredient in terms of strengthening the lipstick. Various oils and fats are used in lipsticks, such as olive oil, mineral oil, cocoa butter, lanolin, and petrolatum.

Lipsticks get their colors from a variety of pigments and lake dyes including, but not limited to bromo acid, D&C Red No. 21, Calcium Lake such as D&C Red 7 and D&C Red 34, and D&C Orange No. 17. Pink lipsticks are made by mixing white titanium dioxide and red shades. Both organic and inorganic pigments are employed.

Lip stains have a water or gel base and may contain alcohol to help the product stay on leaving a matte look. They temporarily saturate the lips with a dye. Usually designed to be waterproof, the product may come with an applicator brush, directly through the applicator, rollerball, or could be applied with a finger. Lip glosses are intended to add shine to the lips and may add a tint of color, as well as being scented or flavored. Lip balms are most often used to moisturize, tint, and protect the lips. Some brands contain sunscreen. Using a priming lip product such as lip balm or chapstick can prevent chapped lips.

Eye Make-up

- **Mascara** is a cosmetic commonly used to enhance the eyelashes. It may darken, thicken, lengthen, and/or define the eyelashes. Normally in one of three forms—liquid, powder, or cream—the modern mascara product has various formulas; however, most contain the same basic components of pigments, oils, waxes, and preservatives. The most common form of mascara is a liquid in a tube.
- **Eye shadow** (or **eyeshadow**) is a cosmetic applied primarily to the eyelids to make the wearer's eyes stand out or look more attractive. Eye shadow can also be applied under eyes or to brow bones.

  Eye shadow can add depth and dimension to one's eyes, complement one's eye color, make one's eyes appear larger, or simply draw attention to the eyes. Eye shadow comes in many different colors and textures. It is usually made from a powder but can also be found in liquid, pencil, cream or mousse form. Just like other trends, eyeshadow looks also have trends.

  Eye shadows typically consist of four types of ingredients: base fillers, binders, slip and preservatives. In order to make eye shadow, there must be a balance between the fillers and binders.

  Base fillers are usually minerals such as mica, talc or kaolin clay, which add bulk and texture to eye shadow. They make up about 30% of eye shadow powders and 25% of cream eye shadows. Mica absorbs moisture, gives the eye shadow shine and luster, and makes it opaque. Mica powders, iron oxides and clays can give color pigments to eye shadows.

  Binders help eye shadow adhere and stay attached to skin. Eye shadows can have dry or liquid binders. Zinc and magnesium, which are both white powders, are commonly used as dry binders. Zinc also adds color and can be used to increase the thickness of the eyeshadow. Silicone, paraffin wax, mineral oil or vegetable oils may be used as liquid binders.

  Slip allows eye shadow to glide across the skin smoothly. Products may use silica or nylon, which are fine, colorless powders. Other types of slip include dimethicone, boron nitride or bismuth oxychloride.

Preservatives help products stay bacteria free and extend their lifespan. Common preservatives in eye shadow are glycol and tocopherol.



Figure **1.7.6** Eyes with heavy gold eye shadow. Source: Wikipedia

Eye liner or **eyeliner** is a cosmetic used to define the eyes. It is applied around the contours of the eye(s) to create a variety of aesthetic effects. It can come in the form of a pencil, a gel, or a liquid and can be found in almost any color. Traditional wax-based eye liners are made from about 20 components. About 50% by weight are waxes (e.g., Japan wax, fats, or related soft materials that easily glide on to the skin. Stearyl heptanoate is found in most cosmetic eyeliner. Typical pigments include black iron oxides, as well as smaller amounts of titanium dioxide and Prussian blue.

Eyebrow shaders, and pencils are often used to define the eyebrow or make it appear fuller. These can create an outline for the brows or mimic hairs where there are sparse areas. Brow gels are also used in creating a thicker brow; they allow for the hairs to be more textured, which gives the appearance of thicker, fuller brows. Lastly, brow powders or even eye shadows are used for those who want a fuller and more natural look, by placing the brow powder or eye shadow (closest to the natural hair color) in areas where there is less hair.

Deodorants and Antiperspirants

A **deodorant** is a substance applied to the body to prevent or mask body odor due to bacterial breakdown of perspiration in the armpits, groin, and feet, and in some cases vaginal secretions. A subclass of deodorants, called **antiperspirants**, prevents sweating itself, typically by blocking sweat glands. Antiperspirants are used on a wider range of body parts, at any place where sweat would be inconvenient or unsafe, since unwanted sweating can interfere with comfort, vision, and grip (due to slipping). Other types of deodorant allow sweating but prevent bacterial action on sweat, since human sweat only has a noticeable smell when it is decomposed by bacteria.

In the United States, the Food and Drug Administration classifies and regulates most deodorants as cosmetics but classifies antiperspirants as over-the-counter drugs.

In the United States, deodorants are classified and regulated as cosmetics by the U.S. Food and Drug Administration (FDA) and are designed to eliminate odor. Deodorants are often alcohol based. Alcohol initially stimulates sweating but may also temporarily kill bacteria. Other active ingredients in deodorants include sodium stearate, sodium chloride, and stearyl alcohol. Deodorants can be formulated with other, more persistent antimicrobials such as triclosan that slow bacterial growth or with metal chelant compounds such as EDTA. Deodorants may contain perfume fragrances or natural essential oils intended to mask the odor of perspiration. In the past, deodorants included chemicals such as zinc oxide, acids, ammonium chloride, sodium bicarbonate, and formaldehyde, but some of these ingredients were messy, irritating to the skin, or even carcinogenic.

Over-the-counter products, often labeled as "natural deodorant crystal", contain the chemical rock crystals potassium alum or ammonium alum, which prevents bacterial action on sweat. These have gained popularity as an alternative health product, in spite of concerns about possible risks related to aluminum (see below – all alum salts contain aluminum in the form of aluminum sulphate salts) and contact dermatitis.

In the United States, deodorants combined with antiperspirant agents are classified as drugs by the FDA. Antiperspirants attempt to stop or significantly reduce perspiration and thus reduce the moist climate in which bacteria thrive. Aluminium chloride, aluminium chlorohydrate, and aluminium-zirconium compounds, most notably aluminium zirconium tetrachlorohydrex gly and aluminium zirconium trichlorohydrex gly, are frequently used in antiperspirants. Aluminium chlorohydrate and aluminium-zirconium tetrachlorohydrate gly are the most frequent active ingredients in commercial antiperspirants. Aluminium-based complexes react with the electrolytes in the sweat to form a gel plug in the duct of the sweat gland. The plugs prevent the gland from excreting

liquid and are removed over time by the natural sloughing of the skin. The metal salts work in another way to prevent sweat from reaching the surface of the skin: the aluminium salts interact with the keratin fibrils in the sweat ducts and form a physical plug that prevents sweat from reaching the skin's surface. Aluminium salts also have a slight astringent effect on the pores; causing them to contract, further preventing sweat from reaching the surface of the skin. The blockage of a large number of sweat glands reduces the amount of sweat produced in the underarms, though this may vary from person to person. Methenamine (Figure **1.7.7**) in the form of cream or spray is effective in the treatment of excessive sweating and attendant odor. Antiperspirants are usually best applied before bed.

Figure **1.7.7** *Methenamine-based antiperspirant for treatment of excessive sweating.*

Toothpaste: Soap with Grit and Flavor

Toothpaste (Figure 1.7.8) is a paste or gel dentifrice used with a toothbrush to clean and maintain the aesthetics and health of teeth. Toothpaste is used to promote oral hygiene: it is an abrasive that aids in removing dental plaque and food from the teeth, assists in suppressing halitosis, and delivers active ingredients (most commonly fluoride) to help prevent tooth decay (dental caries) and gum disease (gingivitis). Salt and sodium bicarbonate (baking soda) are among materials that can be substituted for commercial toothpaste. Large amounts of swallowed toothpaste can be toxic.



Figure 1.7.8 A variety of brands of toothpaste.

In addition to 20%–42% water, toothpastes are derived from a variety of components, the three main ones being abrasives, fluoride, and detergents.

Abrasives constitute at least 50% of a typical toothpaste. These insoluble particles are designed to help remove plaque from the teeth. The removal of plaque and calculus prevents the accumulation of tartar and is widely claimed to help minimize cavities and periodontal disease, although the clinical significance of this benefit is debated. Representative abrasives include particles of aluminum hydroxide ($Al(OH)_3$), calcium carbonate ($CaCO_3$), various calcium hydrogen phosphates, various silicas and zeolites, and hydroxyapatite ($Ca_5(PO_4)_3OH$).

Abrasives, like the dental polishing agents used in dentists' offices, also cause a small amount of enamel erosion which is termed "polishing" action. Some brands contain powdered white mica, which acts as a mild abrasive, and also adds a cosmetically pleasing glittery shimmer to the paste. The polishing of teeth removes stains from tooth surfaces, but has not been shown to improve dental health over and above the effects of the removal of plaque and calculus.

The abrasive effect of toothpaste is indicated by its RDA value. Too high RDA values are deleterious. Some dentists recommend toothpaste with an RDA value no higher than 50 for daily use.

Fluoride in various forms is the most popular active ingredient in toothpaste to prevent cavities. Fluoride is present in small amounts in plants, animals, and some natural water sources. The additional fluoride in toothpaste has beneficial effects on the

formation of dental enamel and bones. Sodium fluoride (NaF) is the most common source of fluoride, but stannous fluoride (SnF_2), olaflur (an organic salt of fluoride), and sodium monofluorophosphate (Na_2PO_3F) are also used. Stannous fluoride has been shown to be more effective than sodium fluoride in reducing the incidence of dental caries and controlling gingivitis, but causes somewhat more surface stains.

Much of the toothpaste sold in the United States has 1,000 to 1,100 parts per million fluoride. In European countries, such as the UK or Greece, the fluoride content is often higher; a NaF content of 0.312% w/w (1,450 ppm fluoride) is common. All of these concentrations are likely to prevent tooth decay, according to a 2019 Cochrane review. Concentrations below 1,000 ppm are not likely to be preventive, and the preventive effect increases with concentration. Clinical trials support the use of high fluoride dentifrices, as it was found to reduce the amount of plaque accumulated, decrease the number of mutans streptococci and lactobacilli and possibly promote calcium fluoride deposits to a higher degree than after the use of traditional fluoride containing dentifrices. However, these effects must be balanced with the increased risk of harm at higher concentrations.

Many, although not all, toothpastes contain sodium lauryl sulfate (SLS) or related **surfactants (detergents)**. SLS is found in many other personal care products as well, such as shampoo, and is mainly a foaming agent, which enables uniform distribution of toothpaste, improving its cleansing power.

Other Components in toothpaste formulations include:

- Antibacterial agents. Triclosan or zinc chloride prevent gingivitis and, according to the American Dental Association, helps reduce tartar and bad breath.
- Flavorants. Toothpaste comes in a variety of colors and flavors intended to encourage use of the product. The three most common flavorants are peppermint, spearmint, and wintergreen.
- Reminalizers. Hydroxyapatite nanocrystals and a variety of calcium phosphates are included in formulations for remineralization, i.e. the reformation of enamel.

Agents are added to suppress the tendency of toothpaste to dry into a powder. Included are various sugar alcohols, such as glycerol, sorbitol, or xylitol, or related derivatives, such as 1,2-propylene glycol and polyethyleneglycol

Strontium chloride or potassium nitrate is included in some toothpastes to reduce sensitivity. Two systemic meta-analysis reviews reported that arginine, and calcium sodium phosphosilicate - CSPS containing toothpastes are also effective in alleviating dentinal hypersensitivity respectively. Another randomized clinical trial found superior effects when both formulas were combined together.

Sodium polyphosphate is added to minimize the formation of tartar. Other example to components in toothpastes is the Biotene, which has proved its efficiency in relieving the symptoms of dry mouth in people who suffer from xerostomia according to the results of two randomized clinical trials.

Chlorohexidine mouthwash has been popular for its positive effect on controlling plaque and gingivitis, however, a systemic review studied the effects of chlorohexidine toothpastes and found insufficient evidence to support its use, tooth surface discoloration was observed as a side effect upon using it, which is considered a negative side effect that can affect patients' compliance.

Sodium hydroxide, also known as lye or caustic soda, is listed as an inactive ingredient in some toothpaste, for example Colgate Total.

Some studies have demonstrated that toothpastes with xylitol as an ingredient are more effective at preventing dental caries in permanent teeth of children than toothpastes containing fluoride alone.

Perfumes, Colognes, and Aftershaves

Perfume (Figure **1.7.9**) is a mixture of fragrant essential oils or aroma compounds, fixatives and solvents, used to give the human body, animals, food, objects, and living-spaces an agreeable scent. Perfume types reflect the concentration of aromatic compounds in a solvent, which in fine fragrance is typically ethanol or a mix of water and ethanol. Various sources differ considerably in the definitions of perfume types. The intensity and longevity of a perfume is based on the concentration, intensity, and longevity of the aromatic compounds, or perfume oils, used. Specific terms are used to describe a fragrance's approximate concentration by the percent of perfume oil in the volume of the final product. The most widespread terms are:

- **parfum** or **extrait**, in English known as perfume extract, pure perfume, or simply perfume: 15–40% aromatic compounds (IFRA: typically ~20%);

- **esprit de parfum** (ESdP): 15–30% aromatic compounds, a seldom used strength concentration in between EdP and perfume;
- **eau de parfum** (EdP) or **parfum de toilette** (PdT) (The strength usually sold as "perfume"): 10–20% aromatic compounds (typically ~15%); sometimes called "eau de perfume" or "millésime"; parfum de toilette is a less common term, most popular in the 1980s, that is generally analogous to eau de parfum;
- **eau de toilette** (EdT): 5–15% aromatic compounds (typically ~10%); This is the staple for most masculine perfumes.
- **eau de Cologne** (EdC): often simply called cologne: 3–8% aromatic compounds (typically ~5%);
- **eau fraiche**: products sold as "splashes", "mists", "veils" and other imprecise terms. Generally these products contain 3% or less aromatic compounds and are diluted with water rather than oil or alcohol.



Figure **1.7.9** A bottle of perfume by Yves Saint Laurent

Perfume is described in a musical metaphor as having three sets of *notes*, making the harmonious scent *accord*. The notes unfold over time, with the immediate impression of the top note leading to the deeper middle notes, and the base notes gradually appearing as the final stage. These notes are created carefully with knowledge of the evaporation process of the perfume.

- **Top notes**: Also called the ***head notes***. The scents that are perceived immediately on application of a perfume. Top notes consist of small, light molecules that evaporate quickly. They form a person's initial impression of a perfume and thus are very important in the selling of a perfume. Examples of top notes include mint, lavender and coriander.
- **Middle notes**: Also referred to as ***heart notes***. The scent of a perfume that emerges just prior to the dissipation of the top note. The middle note compounds form the "*heart*" or main body of a perfume and act to mask the often unpleasant initial impression of base notes, which become more pleasant with time. Examples of middle notes include seawater, sandalwood and jasmine.
- **Base notes**: The scent of a perfume that appears close to the departure of the middle notes. The base and middle notes together are the main theme of a perfume. Base notes bring depth and solidity to a perfume. Compounds of this class of scents are typically rich and "deep" and are usually not perceived until 30 minutes after application. Examples of base notes include tobacco, amber and musk.

The scents in the top and middle notes are influenced by the base notes; conversely, the scents of the base notes will be altered by the types of fragrance materials used as middle notes. Manufacturers who publish perfume notes typically do so with the fragrance components presented as a *fragrance pyramid*, using imaginative and abstract terms for the components listed.

Aftershave is a product applied to skin after shaving. Traditionally it is an alcohol based liquid (splash), but it can be a lotion, gel, or even a paste.

It often contains an antiseptic agent such as denatured alcohol, stearate citrate or witch hazel to prevent infection of cuts, as well as to act as an astringent to reduce skin irritation. Menthol is used in some varieties as well to numb irritated skin.

An alcohol-based aftershave usually causes an immediate stinging sensation after applying it post-shave, with effects sometimes lasting several minutes, but most commonly only for seconds. For this reason, a market consisting of highly differentiated products has been created—some using alcohols, some not.

Aftershave balms are frequently recommended for winter use as they tend to be alcohol free and lotion-like, moisturizing the skin.

Some aftershaves use fragrance or essential oil to enhance scent. Moisturizers—natural and artificial, are often touted as able to soften the skin.

Aftershave is sometimes mistakenly referred to as Eau de Cologne due to the very similar nature of the two products. Some aftershave manufacturers encourage using their fragranced aftershave as if it were cologne, in order to increase sales by encouraging consumers to use it in a more versatile manner, rather than just after a shaving session. Some aftershaves were inspired by a cologne.

Early aftershaves included witch-hazel and bay rum, and have been documented in shaving guides. Both still are sold as aftershaves.

Hairy Chemistry

Hair keratin consists of many protein alpha-helices (Figure **1.7.10**). Three alpha-helices are interwoven into a left-handed coil called a protofibril. Eleven protofibrils are bonded and coiled together to make a microfibril. Hundreds of these microfibrils are cemented into an irregular bundle called a macrofibril. These in turn are mixed with dead and living cells to make a complete strand of hair.

The alpha-helices are extensively cross-linked with disulfide bonds from cysteine. These bonds enable keratin to have a somewhat elastic nature. If the alpha -helices stretch unevenly past each other, the disulfide cross-links return them to the original position when the tension is released.

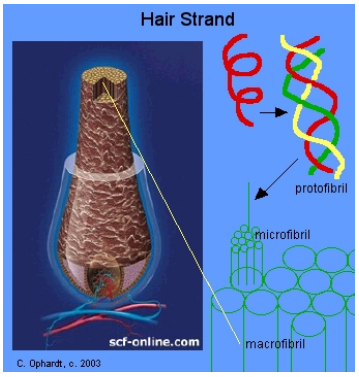


Figure **1.7.10** Protein alpha-helices in a hair strand.

Shampoo

Shampoo (/ʃæmˈpuː/) is a hair care product, typically in the form of a viscous liquid, that is used for cleaning hair. Less commonly, shampoo is available in bar form, like a bar of soap. Shampoo is used by applying it to wet hair, massaging the product into the scalp, and then rinsing it out. Some users may follow a shampooing with the use of hair conditioner.

The typical reason of using shampoo is to remove the unwanted build-up of sebum in the hair without stripping out so much as to make hair unmanageable. Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate or sodium laureth sulfate, with a co-surfactant, most often cocamidopropyl betaine in water. The sulphate ingredient acts as a surfactant, essentially heavy duty soap that makes it easier to trap oil and grease.

Specialty shampoos are marketed to people with dandruff, color-treated hair, gluten or wheat allergies, an interest in using an organic product, and infants and young children ("baby shampoo" is less irritating). There are also shampoos intended for animals that may contain insecticides or other medications to treat skin conditions or parasite infestations such as fleas.

Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate or sodium laureth sulfate, with a co-surfactant, most often cocamidopropyl betaine in water to form a thick, viscous liquid. Other essential ingredients include salt (sodium chloride), which is used to adjust the viscosity, a preservative and fragrance. Other ingredients are generally included in shampoo formulations to maximize the following qualities:

- pleasing foam
- ease of rinsing
- minimal skin and eye irritation

- thick or creamy feeling
- pleasant fragrance
- low toxicity
- good biodegradability
- slight acidity (pH less than 7)
- no damage to hair
- repair of damage already done to hair

Many shampoos are pearlescent. This effect is achieved by the addition of tiny flakes of suitable materials, e.g. glycol distearate, chemically derived from stearic acid, which may have either animal or vegetable origins. Glycol distearate is a wax. Many shampoos also include silicone to provide conditioning benefits.

How Does Shampoo Work?



***Video* 1.7.2** *Shampoo applied to wet hair.*

Hair Coloring

Hair color is the pigmentation of hair follicles due to two types of melanin: eumelanin and pheomelanin. Generally, if more eumelanin is present, the color of the hair is darker; if less eumelanin is present, the hair is lighter. Levels of melanin can vary over time causing a person's hair color to change, and it is possible to have hair follicles of more than one color on the same person. Particular hair colors are often associated with ethnic groups, while gray or white hair is associated with age.

Hair coloring, or **hair dyeing**, is the practice of changing the hair color. The main reasons for this are cosmetic: to cover gray or white hair, to change to a color regarded as more fashionable or desirable, or to restore the original hair color after it has been discolored by hairdressing processes or sun bleaching.

Hair coloring can be done professionally by a hairdresser or independently at home. Today, hair coloring is very popular, with 75% of women and 18% of men living in Copenhagen having reported using hair dye (according to a study by the University of Copenhagen). At-home coloring in the United States reached $1.9 billion in 2011 and was expected to rise to $2.2 billion by 2016.

Hair color can be changed by a chemical process. Hair coloring is classed as "permanent" or "semi-permanent".

Permanent hair color means that the hair's structure has been chemically altered until it is eventually cut away. This does not mean that the synthetic color will remain permanently. During the process, the natural color is removed, one or more shades, and synthetic color has been put in its place. All pigments wash out of the cuticle. Natural color stays in much longer and artificial will fade the fastest (depending on the color molecules and the form of the dye pigments).

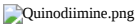
Permanent hair coloring requires three components: (1) 1,4-diaminobenzene (historically) or 2,5-diaminotoluene (currently), (2) a coupling agent, and (3) an oxidant. The process is typically performed under basic conditions. The mechanism of oxidation dyes involves three steps: 1) Oxidation of 1,4-diaminobenzene derivative to the quinone state. 2) Reaction of this diimine with a coupler compound (more detail below). 3) Oxidation of the resulting compound to give the final dye.



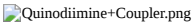
Figure 1.7.11 *Shown here are three red couplers (A, B, C), two yellow-green couplers (D, E) and a blue coupler (F). Couplers are chemical compounds that define the color of the hair dye.*

Steps in Permanent Hair Coloring

The first step shows the oxidation of p-phenylenediamine to the quinonediimine ($C_6H_4(NH)_2$):



The second step involves the attack of this quinonediimine on the coupler.



In the third and final step, the product from the quinonediimine-coupler reaction oxidizes to the final hair dye.



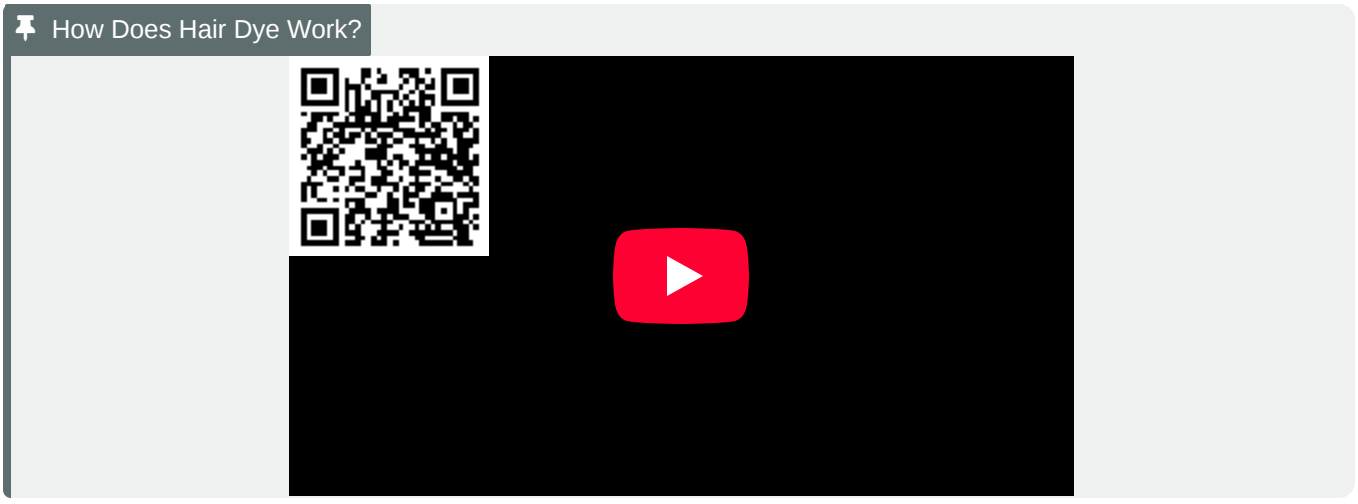
It was once believed that the dye forms in the above reaction bonds to hair permanently. It was later shown that the main reason that this reaction imparts a permanent color on hair by producing larger dye molecules, which is locked inside the hair.

Semi-permanent color washes out over a period of time—typically four to six weeks, so root regrowth is less noticeable. The final color of each strand is affected by its original color and porosity, so there will be subtle variations in color across the head—more natural and less harsh than a permanent dye. However, this means that gray and white hair will not dye to the same color as the rest of the head (in fact, some white hair will not absorb the color at all). A few gray and white hairs will blend in sufficiently not to be noticeable, but as they become more widespread, there will come a point where a semi-permanent alone will not be enough. The move to 100% permanent color can be delayed by using a semi-permanent as a base color, with permanent highlights.

Semi-permanent hair color cannot lighten hair. Hair can only be lightened using chemical lighteners, such as bleach. Bleaching is always permanent because it removes the natural pigment.

"Rinses" are a form of temporary hair color, usually applied to hair during a shampoo and washed out again the next time the hair is wash.

Plant based dyes include henna, indigo and anthocyanin pigments extracted form blackcurrant skin waste.



***Video* 1.7.3** *Applying hair dye.*

Permanent and Temporary Waving

Temporary Wave. When the hair gets wet, water molecules intrude into the keratin strands. The sheer numbers of water molecules are able to disrupt some of the hydrogen bonds which also help to keep the alpha-helices aligned. The helices are able to slip past

each other and will retain a new shape in the hair drying process as new hydrogen bonds are formed. The hair strands are able for a short time to maintain the new curl in the hair.

A **permanent hairstyle**, commonly called a **perm** or "**permanent**" (sometimes called a "perm" to distinguish it from a "straight perm"), is a hairstyle consisting of styles set into the hair. The hairstyle may last a number of months, hence the name.

Perms may be applied using thermal or chemical means. In the latter method, chemicals are applied to the hair, which is then wrapped around forms to produce hairstyles. The same process is used for chemical straightening or relaxing, with the hair being flattened instead of curled during the chemical reaction.

The formation of disulfide bonds has a direct application in producing curls in hair by the permanent wave process. Disulfide bonds Figure 1.7.12 are formed by oxidation of the sulfhydryl groups on cysteine. Different protein chains or loops within a single chain are held together by the strong covalent disulfide bonds. The alpha-helices in the hair strands are bonded by disulfide links.



Figure 1.7.12 Disulfide bonds in hair.

In the permanent wave process, a basic reducing substance (usually ammonium thioglycolate) is first added to reduce and rupture some of the disulfide cross-links, see Figure 1.7.13 below.

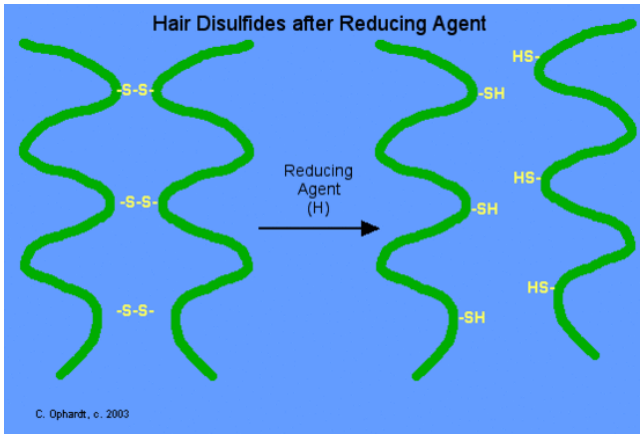


Figure 1.7.13 Addition of a reducing agent to disrupt the disulfide bonds.

The hair is put on rollers or curlers. Since the alpha-helices are no longer tightly cross-linked to each other, the alpha-helices can shift positions in relation to each other. An oxidizing agent, usually a dilute solution of hydrogen peroxide, (also called the neutralizer) is added to reform the disulfide bonds in their new positions (Figure 1.7.14). The permanent will hold these new disulfide bond positions until the hair grows out, since new hair growth is of course not treated.

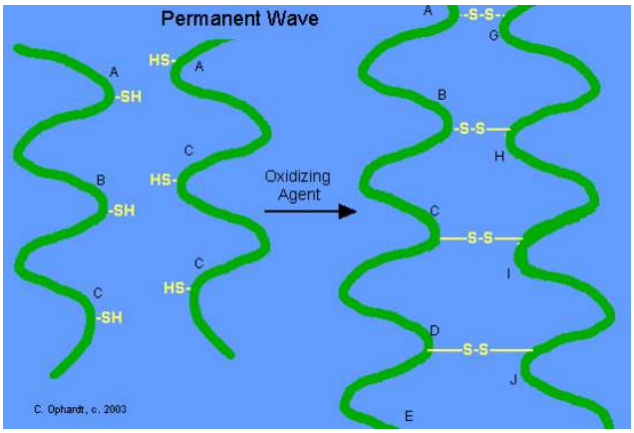


Figure **1.7.14** Addition of a oxidizing agent to reform disulfide bonds.

Hair spray

Hair spray is a common household aqueous solution which is used to stiffen hair into a certain style. It was first developed and manufactured in 1948 by Chase Products, based in Broadview, Illinois. Weaker than hair gel or hair wax, it is sprayed directly onto the hair to hold styles for long periods of time. It sprays evenly over the hair using a pump or aerosol spray nozzle. The product may leave hair feeling 'crunchy' unless brushed out.

The active ingredients in hair spray are called polymers, which keep the hair stiff and firm without snapping. Solvents, which make up most of the content of the hairspray, are responsible for carrying these polymers in a solution.

Originally, the solvent found in hair spray was a chlorofluorocarbon (CFC). CFCs are nontoxic, nonflammable, and make almost ideal aerosol propellants. However, when research concluded that CFCs cause destruction of stratospheric ozone, they were replaced with other solvents, such as alcohols and hydrocarbons.

Hair sprays consist of the following components: concentrate, plasticizers, luster agents, and fragrances, as well as propellants.

One of the polymers used in hair spray is polyvinylpyrrolidone (Figure **1.7.15**) , which is water-soluble. The non-water-soluble polymer polydimethylsiloxane is added to make the hold last a bit longer. Some less common polymers found in hair spray include copolymers with vinyl acetate and copolymers with maleic anhydride.

Figure **1.7.15** Polyvinylpyrrolidone *is a common component of hair spray that confers stiffness to hair.*

Some hair sprays use natural polymers and solvents like vegetable gums dissolved in alcohol. One popular ingredient in natural hair sprays is gum arabic, which is made from the sap of various species of the acacia tree. Gum tragacanth is another herbal gum that is used to stiffen calico and crepe, as well as hair.

Hair Removers

Depilation is the removal of the part of the hair above the surface of the skin. The most common form of depilation is shaving or trimming. Another option is the use of chemical depilatories, which work by breaking the disulfide bonds that link the protein chains that give hair its strength.

A **chemical depilatory** is a cosmetic preparation used to remove hair from the skin. Common active ingredients are salts of thioglycolic acid and thiolactic acids. These compounds break the disulfide bonds in keratin and also hydrolyze the hair so that it is easily removed. Formerly, sulfides such as strontium sulfide were used, but due to their unpleasant odor, they have been replaced by thiols.

The main chemical reaction effected by the thioglycolate is:

2 $HSCH_2CO_2H$ (thioglycolic acid) + R-S-S-R (cystine) → HO_2CCH_2-S-S-CH_2CO_2H (dithiodiglycolic acid) + 2 RSH (cysteine)

Chemical depilatories contain 5–6% calcium thioglycolate in a cream base (to avoid runoff). Calcium hydroxide or strontium hydroxide maintain a pH of about 12. Hair destruction requires about 10 minutes. Depilation is followed by careful rinsing with

water, and various conditioners are applied to restore the skin's pH to normal. Depilation does not destroy the dermal papilla, and the hair grows back.

Chemical depilatories are available in gel, cream, lotion, aerosol, roll-on, and powder forms. Common brands include Nair, Magic Shave and Veet.

Depilatory ointments, or plasters, were known to Greek and Roman authors as *psilothrum*. In Jewish lore, King Solomon is said to have discovered a chemical depilatory made from a mixture of lime and water and orpiment (arsenic trisulfide).

Hair Restorers

Treatments for the various forms of hair loss have only moderate success. Three medications have evidence to support their use in male pattern hair loss: finasteride, dutasteride and minoxidil. They typically work better to prevent further hair loss than to regrow lost hair.

They may be used together when hair loss is progressive or further regrowth is desired after 12 months. Other medications include ketoconazole, and in female androgenic alopecia spironolactone and flutamide. Combinations of finasteride, minoxidil and ketoconazole are more effective than individual use.

Minoxidil is applied topically, is widely used for the treatment of hair loss. It may be effective in helping promote hair growth in both men and women with androgenic alopecia. About 40% of men experience hair regrowth after 3–6 months. It is the only topical product that is FDA approved in America for androgenic hair loss. However, increased hair loss has been reported.

Finasteride is used to treat male pattern hair loss. Treatment provides about 30% improvement in hair loss after six months of treatment, and effectiveness only persists as long as the drug is taken. There is no good evidence for its use in women. It may cause gynecomastia, erectile dysfunction and depression.

Dutasteride is used off label for male pattern hair loss.

There is tentative support for **spironolactopne** in women. Due to its feminising side effects and risk of infertility it is not often used by men. It can also cause low blood pressure, high blood potassium, and abnormal heart rhythms. Also, women who are pregnant or trying to become pregnant generally cannot use the medication as it is a teratogen, and can cause ambiguous genitalia in newborn children.

There is tentative evidence for **flutamide** in women; however, it is associated with relatively high rates of liver problems. Like spironolactone, it is typically only used by women.

Ketoconazole shampoo in conjunction with an oral 5α-reductase inhibitor such as finasteride or dutasteride has been used off label to treat androgenic alopecia.

Summary

- Various personal care products contain ingredients to protect the skin, protect the hair, promote hygiene, for aesthetic purposes etc.
- Temporary and permanent waves are formed due to the disruption and reformation of disulfide bonds in hair strands.

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- Libretext: Human Biology (Wakim and Grewal)
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1.E: Exercises

1.1: Soda Pop Fizz

1.2: Chemicals Compose Ordinary Things

1.3: All Things Are Made of Atoms and Molecules

1.4: The Scientific Method: How Chemists Think

Use the following paragraph to answer the first two questions. In 1928, Sir Alexander Fleming was studying Staphylococcus bacteria growing in culture dishes. He noticed that a mold called Penicillium was also growing in some of the dishes. In Figure 1.13, Petri dish A represents a dish containing only Staphylococcus bacteria. The red dots in dish B represent Penicillium colonies. Fleming noticed that a clear area existed around the mold because all the bacteria grown in this area had died. In the culture dishes without the mold, no clear areas were present. Fleming suggested that the mold was producing a chemical that killed the bacteria. He decided to isolate this substance and test it to see if it would kill bacteria. Fleming grew some Penicillium mold in a nutrient broth. After the mold grew in the broth, he removed all the mold from the broth and added the broth to a culture of bacteria. All the bacteria died.

1. Which of the following statements is a reasonable expression of Fleming's hypothesis?
    a. Nutrient broth kills bacteria.
    b. There are clear areas around the Penicillium mold where Staphylococcus doesn't grow.
    c. Mold kills bacteria.
    d. Penicillium mold produces a substance that kills Staphylococcus.
    e. Without mold in the culture dish, there were no clear areas in the bacteria.
2. Fleming grew Penicillium in broth, then removed the Penicillium and poured the broth into culture dishes containing bacteria to see if the broth would kill the bacteria. What step in the scientific method does this represent?
    a. Collecting and organizing data
    b. Making a hypothesis
    c. Testing a hypothesis by experiment
    d. Rejecting the old hypothesis and making a new one
    e. None of these

A scientific investigation is NOT valid unless every step in the scientific method is present and carried out in the exact order listed in this chapter.

a. True
b. False

Which of the following words is closest to the same meaning as *hypothesis*?

a. fact
b. law
c. formula
d. suggestion
e. conclusion

Why do scientists sometimes discard theories?

a. the steps in the scientific method were not followed in order
b. public opinion disagrees with the theory
c. the theory is opposed by the church
d. contradictory observations are found
e. congress voted against it

Gary noticed that two plants which his mother planted on the same day, that were the same size when planted, were different in size after three weeks. Since the larger plant was in the full sun all day and the smaller plant was in the shade of a tree most of the day,

Gary believed the sunshine was responsible for the difference in the plant sizes. In order to test this, Gary bought ten small plants of the same size and type. He made sure they had the same size and type of pot. He also made sure they had the same amount and type of soil. Then Gary built a frame to hold a canvas roof over five of the plants while the other five were nearby but out in the sun. Gary was careful to make sure that each plant received exactly the same amount of water and plant food every day.

1. Which of the following is a reasonable statement of Gary's hypothesis?
    a. Different plants have different characteristics.
    b. Plants that get more sunshine grow larger than plants that get less sunshine.
    c. Plants that grow in the shade grow larger.
    d. Plants that don't receive water will die.
    e. Plants that receive the same amount of water and plant food will grow the same amount.
2. What scientific reason might Gary have for insisting that the container size for the all plants be the same?
    a. Gary wanted to determine if the size of the container would affect the plant growth.
    b. Gary wanted to make sure the size of the container did not affect differential plant growth in his experiment.
    c. Gary want to control how much plant food his plants received.
    d. Gary wanted his garden to look organized.
    e. There is no possible scientific reason for having the same size containers.
3. What scientific reason might Gary have for insisting that all plants receive the same amount of water everyday?
    a. Gary wanted to test the effect of shade on plant growth and therefore, he wanted to have no variables other than the amount of sunshine on the plants.
    b. Gary wanted to test the effect of the amount of water on plant growth.
    c. Gary's hypothesis was that water quality was affecting plant growth.
    d. Gary was conserving water.
    e. There is no possible scientific reason for having the same amount of water for each plant every day.
4. What was the variable being tested in Gary's experiment?
    a. the amount of water
    b. the amount of plant food
    c. the amount of soil
    d. the amount of sunshine
    e. the type of soil
5. Which of the following factors may be varying in Gary's experimental setup that he did not control?
    a. individual plant variation
    b. soil temperature due to different colors of containers
    c. water loss due to evaporation from the soil
    d. the effect of insects which may attack one set of plants but not the other
    e. All of the above are possible factors that Gary did not control.

When a mosquito sucks blood from its host, it penetrates the skin with its sharp beak and injects an anti-coagulant so the blood will not clot. It then sucks some blood and removes its beak. If the mosquito carries disease-causing microorganisms, it injects these into its host along with the anti-coagulant. It was assumed for a long time that the virus typhus was injected by the louse when sucking blood in a manner similar to the mosquito. But apparently this is not so. The infection is not in the saliva of the louse, but in the feces. The disease is thought to be spread when the louse feces come in contact with scratches or bite wounds in the host's skin. A test of this was carried out in 1922 when two workers fed infected lice on a monkey, taking great care that no louse feces came into contact with the monkey. After two weeks, the monkey had NOT become ill with typhus. The workers then injected the monkey with typhus and it became ill within a few days. Why did the workers inject the monkey with typhus near the end of the experiment?

a. to prove that the lice carried the typhus virus
b. to prove the monkey was similar to man
c. to prove that the monkey was not immune to typhus

d. to prove that mosquitoes were not carriers of typhus
e. the workers were mean

Eijkman fed a group of chickens exclusively on rice whose seed coat had been removed (polished rice or white rice). The chickens all developed polyneuritis (a disease of chickens) and died. He fed another group of chickens unpolished rice (rice that still had its seed coat). Not a single one of them contracted polyneuritis. He then gathered the polishings from rice (the seed coats that had been removed) and fed the polishings to other chickens that were sick with polyneuritis. In a short time, the birds all recovered. Eijkman had accurately traced the cause of polyneuritis to a faulty diet. For the first time in history, a food deficiency disease had been produced and cured experimentally. Which of the following is a reasonable statement of Eijkman's hypothesis?

a. Polyneuritis is a fatal disease for chickens.
b. White rice carries a virus for the disease polyneuritis.
c. Unpolished rice does not carry the polyneuritis virus.
d. The rice seed coat contains a nutrient that provides protection for chickens against polyneuritis.
e. None of these is a reasonable statement of Eijkman's hypothesis.

The three questions below relate to the following paragraphs.

Scientist A noticed that in a certain forest area, the only animals inhabiting the region were giraffes. He also noticed that the only food available for the animals was on fairly tall trees and as the summer progressed, the animals ate the leaves high and higher on the trees. The scientist suggested that these animals were originally like all other animals but generations of animals stretching their necks to reach higher up the trees for food, caused the species to grow very long necks.

Scientist B conducted experiments and observed that stretching muscles does NOT cause bones to grow longer nor change the DNA of animals so that longer muscles would be passed on to the next generation. Scientist B, therefore, discarded Scientist A's suggested answer as to why all the animals living in the area had long necks. Scientist B suggested instead that originally many different types of animals including giraffes had lived in the region but only the giraffes could survive when the only food was high in the trees, and so all the other species had left the area.

1. Which of the following statements is an interpretation, rather than an observation?
   A. The only animals living in the area were giraffes.
   B. The only available food was on tall trees.
   C. Animals which constantly stretch their necks will grow longer necks.
   D. A, B, and C are all interpretations.
   E. A, B, and C are all observations.
2. Scientist A's hypothesis was that
   A. the only animals living in the area were giraffes.
   B. the only available food was on tall trees.
   C. animals which constantly stretch their necks will grow longer necks.
   D. the animals which possess the best characteristics for living in an area, will be the predominant species.
   E. None of the above are reasonable statements of Scientist A's hypothesis.
3. Scientist A's hypothesis being discarded is
   A. evidence that the scientific method doesn't always work.
   B. a result achieved without use of the scientific method.
   C. an example of what happened before the scientific method was invented.
   D. an example of the normal functioning of the scientific method.
   E. an unusual case.

When a theory has been known for a long time, it becomes a law.

a. True
b. False

During Pasteur's time, anthrax was a widespread and disastrous disease for livestock. Many people whose livelihood was raising livestock lost large portions of their herds to this disease. Around 1876, a horse doctor in eastern France named Louvrier, claimed

to have invented a cure for anthrax. The influential men of the community supported Louvrier's claim to have cured hundreds of cows of anthrax. Pasteur went to Louvrier's hometown to evaluate the cure. The cure was explained to Pasteur as a multi-step process during which: 1) the cow was rubbed vigorously to make her as hot as possible; 2) long gashes were cut into the cows skin and turpentine was poured into the cuts; 3) an inch-thick coating of cow manure mixed with hot vinegar was plastered onto the cow and the cow was completely wrapped in a cloth. Since some cows recover from anthrax with no treatment, performing the cure on a single cow would not be conclusive, so Pasteur proposed an experiment to test Louvrier's cure. Four healthy cows were to be injected with anthrax microbes, and after the cows became ill, Louvrier would pick two of the cows (A and B) and perform his cure on them while the other two cows (C and D) would be left untreated. The experiment was performed and after a few days, one of the untreated cows died and one of them got better. Of the cows treated by Louvrier's cure, one cow died and one got better. In this experiment, what was the purpose of infecting cows C and D?

a. So that Louvrier would have more than two cows to choose from.
b. To make sure the injection actually contained anthrax.
c. To serve as experimental controls (a comparison of treated to untreated cows).
d. To kill as many cows as possible.

A hypothesis is

a. a description of a consistent pattern in observations.
b. an observation that remains constant.
c. a theory that has been proven.
d. a tentative explanation for a phenomenon.

A number of people became ill after eating oysters in a restaurant. Which of the following statements is a hypothesis about this occurrence?

a. Everyone who ate oysters got sick.
b. People got sick whether the oysters they ate were raw or cooked.
c. Symptoms included nausea and dizziness.
d. The cook felt really bad about it.
e. Bacteria in the oysters may have caused the illness.

Which statement best describes the reason for using experimental controls?

a. Experimental controls eliminate the need for large sample sizes.
b. Experimental controls eliminate the need for statistical tests.
c. Experimental controls reduce the number of measurements needed.
d. Experimental controls allow comparison between groups that are different in only one independent variable.

A student decides to set up an experiment to determine the relationship between the growth rate of plants and the presence of detergent in the soil. He sets up 10 seed pots. In five of the seed pots, he mixes a precise amount of detergent with the soil and the other five seed pots have no detergent in the soil. The five seed pots with detergent are placed in the sun and the five seed pots with no detergent are placed in the shade. All 10 seed pots receive the same amount of water and the same number and type of seeds. He grows the plants for two months and charts the growth every two days. What is wrong with his experiment?

a. The student has too few pots.
b. The student has two independent variables.
c. The student has two dependent variables.
d. The student has no experimental control on the soil.

A scientist plants two rows of corn for experimentation. She puts fertilizer on row 1 but does not put fertilizer on row 2. Both rows receive the same amount of sun and water. She checks the growth of the corn over the course of five months. What is acting as the control in this experiment?

a. Corn without fertilizer.
b. Corn with fertilizer.
c. Amount of water.

d. Height of corn plants.

If you have a control group for your experiment, which of the following is true?

a. There can be more than one difference between the control group and the test group, but not more three differences, or else the experiment is invalid.
b. The control group and the test group may have many differences between them.
c. The control group must be identical to the test group except for one variable.
d. None of these are true.

If the hypothesis is rejected by the experiment, then:

a. the experiment may have been a success.
b. the experiment was a failure.
c. the experiment was poorly designed.
d. the experiment didn't follow the scientific method.

A well-substantiated explanation of an aspect of the natural world is a:

a. theory.
b. law.
c. hypothesis.
d. None of these.

1.5: A Beginning Chemist: How to Succeed

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CHAPTER OVERVIEW

2: Measurement and Problem Solving

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Chemistry, like all sciences, is quantitative. It concerns quantities, things that have amounts and units. Dealing with quantities and relating them to one another is very important in chemistry. In this chapter, we will discuss how we deal with numbers and units, including how they are combined and manipulated.

2.1: Taking Measurements

2.2: Scientific Notation - Writing Large and Small Numbers

2.3: Significant Figures - Writing Numbers to Reflect Precision

2.4: Significant Figures in Calculations

2.5: The Basic Units of Measurement

2.6: Problem Solving and Unit Conversions

2.7: Density

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2.1: Taking Measurements

Learning Objectives

- Express quantities properly, using a number and a unit.

A coffee maker's instructions tell you to fill the coffee pot with 4 cups of water and to use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure **2.1.1**); the nurse is also measuring.



Figure **2.1.1**: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GFDL; Pia von Lützau).

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

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

Example 2.1.1

Identify the number and the unit in each quantity.

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

Solution

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

Key Take Away

- Identify a quantity properly with a number and a unit.

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2.2: Scientific Notation - Writing Large and Small Numbers

Learning Objectives

- Express a large number or a small number in scientific notation.
- Carry out arithmetical operations and express the final answer in scientific notation

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

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

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

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

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

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example **2.2.1**.

Example 2.2.1: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

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

Solution

Solutions to Example 2.2.1

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

Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example **2.2.2** illustrates how to do this.

Example 2.2.2: Expressing Sums and Differences in Scientific Notation

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

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

Solution

Solutions to Example 2.2.2.

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

Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n. Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Example **2.2.3**.

Example 2.2.3: Expressing Products and Quotients in Scientific Notation

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

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

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

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

Solution

Solution to Example 2.2.3

	Explanation	
a	In multiplication, we add the exponents: $(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21}$ In converting 38.7×10^{21} to scientific notation, n has become more positive by 1 because the value of N has decreased.	3.87×10^{22}
b	In division, we subtract the exponents: $\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4}$ In converting 0.183×10^{4} to scientific notation, n has become more negative by 1 because the value of N has increased.	1.83×10^{3}
c	This problem has both multiplication and division: $\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$	4.7×10^{-31}

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2.3: Significant Figures - Writing Numbers to Reflect Precision

Learning Objectives

- Identify the number of significant figures in a reported value.

The **significant figures** in a measurement consist of all the certain digits in that measurement plus one uncertain or estimated digit. In the ruler illustration below, the bottom ruler gave a length with 2 significant figures, while the top ruler gave a length with 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported. With either ruler, it would not be possible to report the length at $2.553\ \text{cm}$ as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.

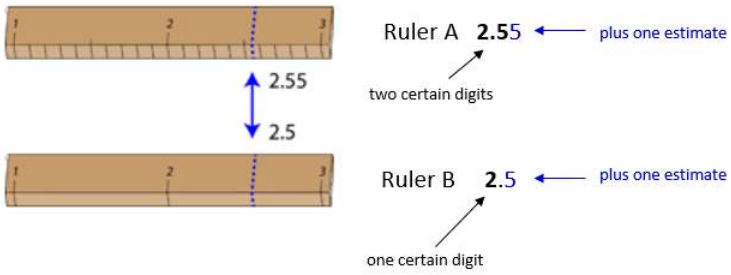


Figure 2.3.1: Measurement with two different rulers.
Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

Measurement Uncertainty

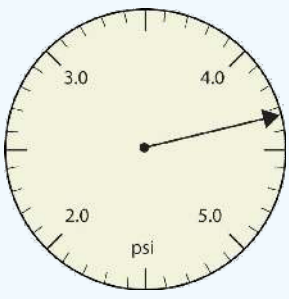
Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest $0.1\ \text{g}$, other highly sensitive balances are capable of measuring to the nearest $0.001\ \text{g}$ or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure 2.3.1 shows two rulers making the same measurement of an object (indicated by the blue arrow).

With either ruler, it is clear that the length of the object is between 2 and $3\ \text{cm}$. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as $2.5\ \text{cm}$. However, another person may judge that the measurement is $2.4\ \text{cm}$ or perhaps $2.6\ \text{cm}$. While the 2 is known for certain, the value of the tenths digit is uncertain.

The top ruler contains marks for tenths of a centimeter (millimeters). Now the same object may be measured as $2.55\ \text{cm}$. The measurer is capable of estimating the hundredths digit because he can be certain that the tenths digit is a 5. Again, another measurer may report the length to be $2.54\ \text{cm}$ or $2.56\ \text{cm}$. In this case, there are two certain digits (the 2 and the 5), with the hundredths digit being uncertain. Clearly, the top ruler is a superior ruler for measuring lengths as precisely as possible.

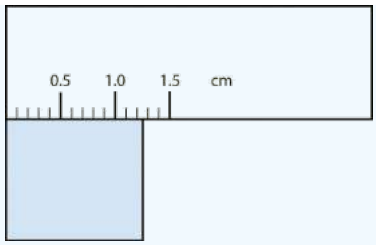
Example 2.3.1: Reporting Measurements to the Proper Number of Significant Figures

Use each diagram to report a measurement to the proper number of significant figures.



a.

b.



Ruler measuring a rectangle in units of centimeters, with the rectangle's edge between 1.2 and 1.3 cm marks

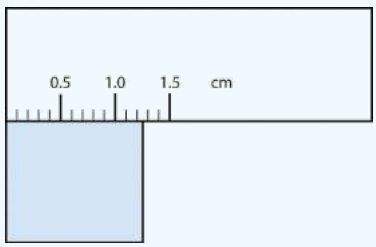
Solutions

Solutions to Example 2.3.1

	Explanation	Answer
a.	The arrow is between 4.0 and 5.0, so the measurement is at least 4.0. The arrow is between the third and fourth small tick marks, so it's at least 0.3. We will have to estimate the last place. It looks like about one-third of the way across the space, so let us estimate the hundredths place as 3. The symbol psi stands for "pounds per square inch" and is a unit of pressure, like air in a tire. The measurement is reported to three significant figures.	4.33 psi
b.	The rectangle is at least 1.0 cm wide but certainly not 2.0 cm wide, so the first significant digit is 1. The rectangle's width is past the second tick mark but not the third; if each tick mark represents 0.1, then the rectangle is at least 0.2 in the next significant digit. We have to estimate the next place because there are no markings to guide us. It appears to be about halfway between 0.2 and 0.3, so we will estimate the next place to be a 5. Thus, the measured width of the rectangle is 1.25 cm. The measurement is reported to three significant figures.	1.25 cm

? Exercise 2.3.1

What would be the reported width of this rectangle?



Answer

1.25 cm

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. The table below details the rules for determining the number of significant figures in a reported measurement. For the examples in the table, assume that the quantities are correctly reported values of a measured quantity.

Table **2.3.1**: Significant Figure Rules

Rule	Examples
1. All nonzero digits in a measurement are significant.	• 237 has three significant figures. • 1.897 has four significant figures.
2. Zeros that appear between other nonzero digits (middle zeros) are always significant.	• 39,004 has five significant figures. • 5.02 has three significant figures.
3. Zeros that appear in front of all of the nonzero digits are called leading zeros. Leading zeros are never significant.	• 0.008 has one significant figure. • 0.000416 has three significant figures.
4. Zeros that appear after all nonzero digits are called trailing zeros. A number with trailing zeros that lacks a decimal point may or may not be significant. **Use scientific notation to indicate the appropriate number of significant figures.**	• 1400 is ambiguous. ◦ 1.4×10^3 has two significant figures. ◦ 1.40×10^3 three significant figures. ◦ 1.400×10^3 has four significant figures.
5. Trailing zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point.	• 620.0 has four significant figures. • 19.000 has five significant figures.

Exact Numbers

Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000…). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

Example 2.3.2

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

a. 5.87
b. 0.031
c. 52.90
d. 00.2001
e. 500
f. 6 atoms

Solution

Solution to Example 2.3.2

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

? Exercise 2.3.2

Give the number of significant figures in each.

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

Answer a

three significant figures

Answer b

four significant figures

Answer c

four significant figures

Answer d

infinite (exact number)

Answer e

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

Accuracy and Precision

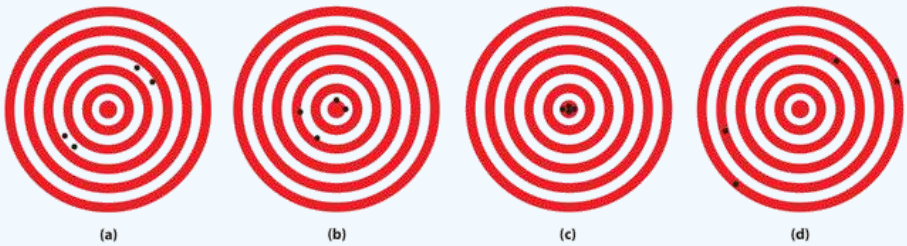
Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise. The video below demonstrates the concepts of accuracy and precision.



Video **2.3.1**: Difference between precision and accuracy.

Example 2.3.3

The following archery targets show marks that represent the results of four sets of measurements.



Which target shows

a. a precise, but inaccurate set of measurements?
b. a set of measurements that is both precise and accurate?
c. a set of measurements that is neither precise nor accurate?

Solution

a. Set **(a)** is precise, but inaccurate.
b. Set **(c)** is both precise and accurate.
c. Set **(d)** is neither precise nor accurate.

Summary

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

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2.4: Significant Figures in Calculations

Learning Objectives

- Use significant figures correctly in arithmetical operations.

Rounding

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

Consider the measurement **207.518 m**. Right now, the measurement contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table **2.4.1**.

Table **2.4.1**: Rounding examples

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

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

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

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

Multiplication and Division

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

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

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

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

Example 2.4.1

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

a. 23.096×90.300
b. 125×9.000

Solution

a

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

b

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

Addition and Subtraction

How are significant figures handled in calculations? It depends on what type of calculation is being performed. If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. For example, if you were to add 1.2 and 4.71, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$\begin{array}{l} 1.2 \\ \underline{4.41} \\ 5.61 \\ \quad \uparrow \text{ limit final answer to the tenths column: } 5.6 \end{array}$$

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

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

$$\begin{array}{l} 77.2 \\ \underline{10.46} \\ 87.66 \\ \quad \uparrow \text{ limit final answer to the tenths column and round up: } 87.7 \end{array}$$

Example 2.4.2

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

Solution

a

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

b

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

Exercise 2.4.2

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

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

Answer a:

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

Answer b:

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

Answer c:

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

Answer d:

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

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

Calculations Involving Multiplication/Division and Addition/Subtraction

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate rounding needs to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.



Video 2.4.1: Significant figures in mixed operations (https://www.youtube.com/watch?v=yBntMndXQWA).



Video 2.4.2: https://www.youtube.com/watch?v=__csP0NtlGI

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.

Example 2.4.3

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

Solution

a.

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

b.

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

c.

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

Exercise 2.4.3

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

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

Answer a

-5.62 s

Answer b

110.2 cm

Summary

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

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2.5: The Basic Units of Measurement

Learning Objectives

- State the different measurement systems used in chemistry.
- Describe how prefixes are used in the metric system and identify how the prefixes milli-, centi-, and kilo- compare to the base unit.

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

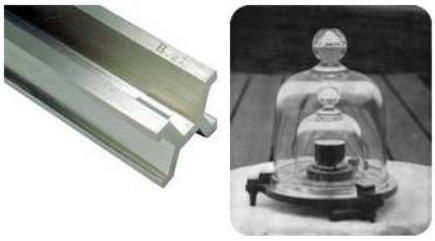


Figure **2.5.1**: Meter standard (left) and Kilogram standard (right).

SI Base Units

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units in Table **2.5.1**.

Table **2.5.1**: SI Base Units of Measurement

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

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

Unfortunately, the Metric System is Not Ubiquitous

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

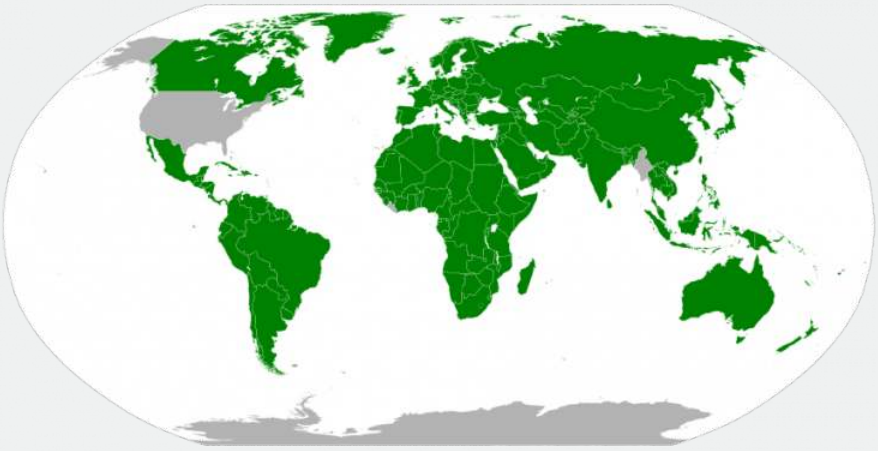


Figure 2.5.1: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

Prefix Multipliers

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word μεγας, meaning "great". Table 2.5.2 lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

Table 2.5.2: SI Prefixes

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

There are a couple of odd little practices with the use of metric abbreviations. Most abbreviations are lowercase. We use "**m**" for meter and not "**M**". However, when it comes to volume, the base unit "liter" is abbreviated as "**L**" and not "**l**". So we would write 3.5 milliliters as **3.5 mL**.

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

Example 2.5.1: Unit Abbreviations

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

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

Solutions

Solutions to Example 2.5.1

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

Exercise 2.5.1

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

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

Answer a:

km

Answer b:

mg

Answer c:

ns

Answer d:

cL

Summary

- Metric prefixes derive from Latin or Greek terms. The prefixes are used to make the units manageable.
- The SI system is based on multiples of ten. There are seven basic units in the SI system. Five of these units are commonly used in chemistry.

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2.6: Problem Solving and Unit Conversions

Learning Objectives

- To convert a value reported in one unit to a corresponding value in a different unit using conversion factors.

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

Converting Between Units with Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can convert meters into centimeters, or a more complex one can convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. Always remember that a conversion factor has to represent a fact; this fact can either be simple or more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you are working with (Table 2.6.1).

Table 2.6.1: Conversion Factors from SI units to English Units

English Units	Metric Units	Quantity
1 ounce (oz)	28.35 grams (g)	*mass
1 fluid once (oz)	29.6 mL	volume
2.205 pounds (lb)	1 kilogram (kg)	*mass
1 inch (in)	2.54 centimeters (cm)	length
0.6214 miles (mi)	1 kilometer (km)	length
1 quarter (qt)	0.95 liters (L)	volume

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

Of course, there are other ratios which are not listed in Table 2.6.1. They may include:

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

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

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

or

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

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

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

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

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

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

Performing Dimensional Analysis

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

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

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

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

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

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

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

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

quantity (in old units) × conversion factor = quantity (in new units)

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

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

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

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure **2.6.1** shows a concept map for constructing a proper conversion.

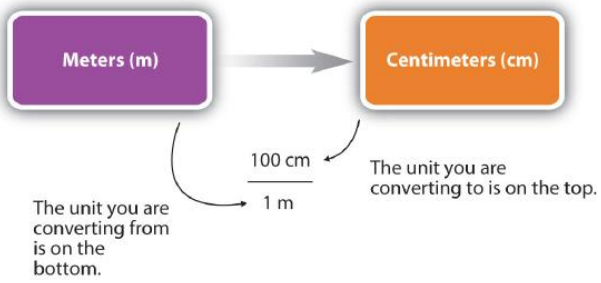


Figure 2.6.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

General Steps in Performing Dimensional Analysis

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

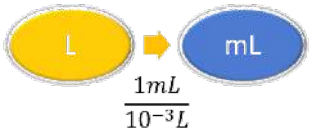
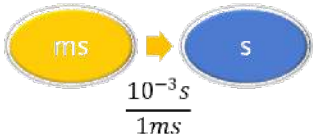
Significant Figures in Conversions

How do conversion factors affect the determination of significant figures?

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

Example 2.6.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

	Example 2.6.1	Example 2.6.2
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?	A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: mL	Given: 18 ms Find: s
List other known quantities.	$1\,mL = 10^{-3}L$	$1\,ms = 10^{-3}s$
Prepare a concept map and use the proper conversion factor.	 $\frac{1mL}{10^{-3}L}$	 $\frac{10^{-3}s}{1ms}$
Cancel units and calculate.	$4.7\cancel{L} \times \frac{1\text{ mL}}{10^{-3}\ \cancel{L}} = 4,700\text{ mL}$ or $4.7\cancel{L} \times \frac{1,000\text{ mL}}{1\ \cancel{L}} = 4,700\text{ mL}$ or 4.7 x 10^3 2SF, not ambiguous	$18\ \cancel{ms} \times \frac{10^{-3}\text{ s}}{1\ \cancel{ms}} = 0.018\text{ s}$ or $18\ \cancel{ms} \times \frac{1\text{ s}}{1,000\ \cancel{ms}} = 0.018\text{ s}$
Think about your result.	The amount in mL should be 1000 times larger than the given amount in L.	The amount in s should be 1/1000 the given amount in ms.

? Exercise 2.6.1

Perform each conversion.

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

Answer a:

$1.01000x10^{-4}s$

Answer b:

$3.208x10^{4}g$

Answer c:

$1.53x10^{2}cg$

Summary

- Conversion factors are used to convert one unit of measurement into another.
- Dimensional analysis (unit conversions) involves the use of conversion factors that will cancel unwanted units and produce the appropriate units.

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2.7: Density

Learning Objectives

- Define density.
- Use density as a conversion factor.

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

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

or just

$$\rho = \frac{m}{V} \tag{2.7.1}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relationship of mass and volume. Pure water, for example, has a density of 0.998 g/cm^3 at 25° C. The average densities of some common substances are in Table **2.7.1**. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table **2.7.1**: Densities of Common Substances

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

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

Example 2.7.1: Ethyl Alcohol

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

Solution

This is a direct application of Equation **2.7.1**:

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

? Exercise 2.7.1

a. Find the density (in kg/L) of a sample that has a volume of 36.5 L and a mass of 10.0 kg.
b. If you have a 2.130 mL sample of acetic acid with mass 0.002234 kg, what is the density in kg/L?

Answer a

$0.274\ kg/L$

Answer b

$1.049\ kg/L$

Density as a Conversion Factor

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

$$\frac{13.6\ g}{1\ mL} = 1$$

and

$$\frac{1\ mL}{13.6\ g} = 1$$

Which one do we use? It depends, as usual, on the units we need to cancel and introduce. For example, suppose we want to know the mass of 2.0 mL of mercury. We would use the conversion factor that has milliliters on the bottom (so that the milliliter unit cancels) and grams on top, so that our final answer has a unit of mass:

$$2.0\ \cancel{mL} \times \frac{13.6\ g}{1\ \cancel{mL}} = 27.2\ g = 27\ g$$

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

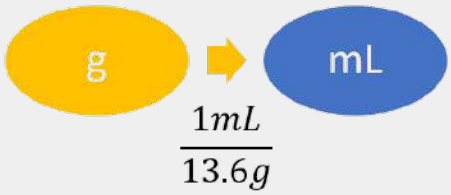
> *Density can be used as a conversion factor between mass and volume.*

✓ Example 2.7.2: Mercury Thermometer Steps for Problem Solving

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

Solution

Solution to Example 2.9.2

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 0.750 g Find: mL
List other known quantities.	13.6 g/mL (density of mercury)
Prepare a concept map.	
Calculate.	$0.750\ \cancel{g} \times \frac{1\ \text{mL}}{13.6\ \cancel{g}} = 0.055147...\ \text{mL} \approx 0.0551\ \text{mL}$ We have limited the final answer to three significant figures.

? Exercise 2.7.2

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

Answer

$77\ L$

Summary

- Density is defined as the mass of an object divided by its volume.
- Density can be used as a conversion factor between mass and volume.

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CHAPTER OVERVIEW

3: Matter and Energy

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3.4: Classifying Matter According to Its Composition
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3.6: Changes in Matter - Physical and Chemical Changes
3.7: Conservation of Mass - There is No New Matter
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3.10: Temperature - Random Motion of Molecules and Atoms

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3.1: In Your Room

Matter is any substance that has mass and takes up space. Matter includes atoms and anything made up of atoms, but not other energy phenomena or waves such as light or sound. While this simple definition is easily applied, the way people view matter is often broken down into two characteristic length scales: the macroscopic and the microscopic.



Figure **3.1.1**: A typical American university and college dormitory room in 2002 (CC BY-SA 3.0; Raul654).

The macroscopic scale is the length scale on which objects or phenomena are large enough to be visible almost practically with the naked eye, without magnifying optical instruments. Everything that one can see, touch, and handle in the dorm room of Figure **3.1.1** is within the macroscopic scale. To describe each of these objects, only a few macroscopic properties are required. However, each of these items can be decomposed into smaller microscopic scale properties.

The microscopic scale is the scale of objects and events smaller than those that can easily be seen by the naked eye, requiring a lens or microscope to see them clearly. All of the everyday objects that we can bump into, touch, or squeeze are ultimately composed of atoms. This ordinary atomic matter is in turn made up of interacting subatomic particles—usually a nucleus of protons and neutrons, and a cloud of orbiting electrons. Because of this, a large number of variables are needed to describe such a system which complicates the characterization.

Matter vs. Mass

Matter should not be confused with mass, as the two are not the same in modern physics. Matter is a physical substance of which systems may be composed, while mass is not a substance, but rather a quantitative property of matter and other substances or systems.

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3.2: What is Matter?

Learning Objectives

- Define matter and explain how it is composed of building blocks known as "atoms".

We are all familiar with matter. The definition of **Matter** is anything that has mass and volume (takes up space). For most common objects that we deal with every day, it is fairly simple to demonstrate that they have mass and take up space. You might be able to imagine, however, the difficulty for people several hundred years ago to demonstrate that air had mass and volume. Air (and all other gases) are invisible to the eye, have very small masses compared to equal amounts of solids and liquids, and are quite easy to compress (change volume). Without sensitive equipment, it would have been difficult to convince people that gases are matter. Today, we can measure the mass of a small balloon when it is deflated and then blow it up, tie it off, and measure its mass again to detect the additional mass due to the air inside. The mass of air, under room conditions, that occupies a one quart jar is approximately 0.0002 pounds. This small amount of mass would have been difficult to measure in times before balances were designed to accurately measure very small masses. Later, scientists were able to compress gases into such a small volume that the gases turned into liquids, which made it clear that gases are matter.



Figure 3.2.1: Everything from an ant, to a truck, to the earth, and even the entire galaxy is composed of matter. Images used with permission from Wikipedia (CC_SA-BY-3.0; credit High Contrast).

Even though the universe consists of "things" as wildly different as ants and galaxies, the matter that makes up all of these "things" is composed of a very limited number of building blocks. These building blocks are known as **atoms**, and so far, scientists have discovered or created a grand total of 118 different types of atoms. Scientists have given a name to each different type of atom. A substance that is composed of only one type of atom is called an element. At this point, what should amaze you is that all forms of matter in our universe are made with only 118 different building blocks. In some ways, it's sort of like cooking a gourmet, five-course meal using only three ingredients! How is it possible? To answer that question, you have to understand the ways in which different elements are put together to form matter.

The most important method that nature uses to organize atoms into matter is the formation of **molecules**. Molecules are groups of two or more atoms that have been bonded together. There are millions of different ways to bond atoms together, which means that

there are millions of different possible molecules. Each of these molecules has its own set of chemical properties, and it's these properties with which chemists are most concerned. You will learn a lot more about atoms and molecules, including how they were discovered, in a later part of the textbook.

Summary

All matter has mass and occupies space. All physical objects are made of matter. Matter itself is composed of tiny building blocks known as "atoms". There are only 118 different types of atoms known to man. Frequently, atoms are bonded together to form "molecules".

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3.3: Classifying Matter According to Its State—Solid, Liquid, and Gas

Learning Objectives

- To describe the solid, liquid and gas phases.

Water can take many forms. At low temperatures (below **0°C**), it is a solid. When at "normal" temperatures (between **0°C** and **100°C**), it is a liquid. While at temperatures above **100°C**, water is a gas (steam). The state that water is in depends upon the temperature. Each state has its own unique set of physical properties. Matter typically exists in one of three states: **solid**, **liquid**, or **gas**.

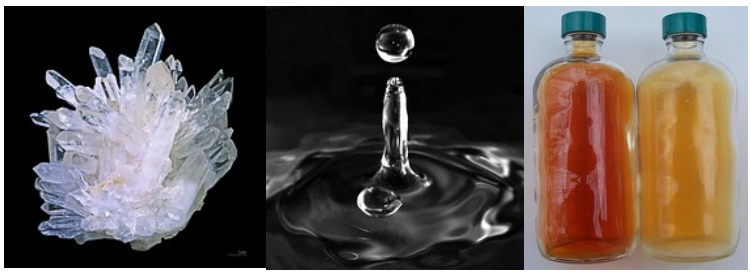


Figure **3.3.1**: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

The state that a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states. Figure **3.3.2** shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

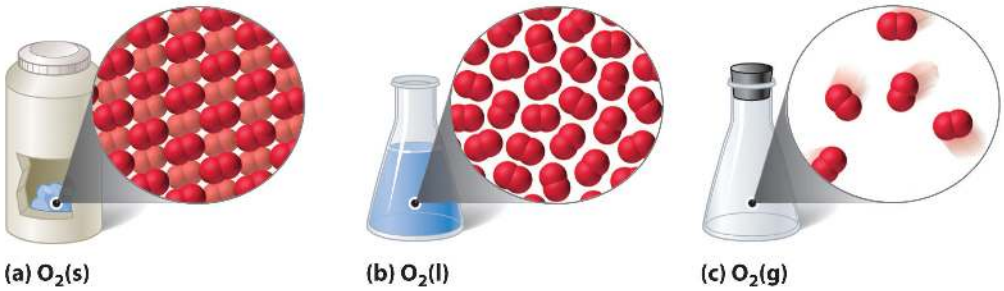
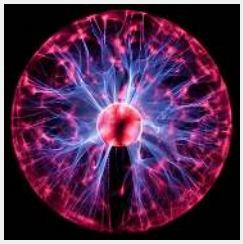


Figure **3.3.2**: A Representation of the Solid, Liquid, and Gas States. (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

Plasma: A Fourth State of Matter

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



A plasma globe operating in a darkened room. (CC BY-SA 3.0; Chocolateoak).

Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.

Solids are defined by the following characteristics:

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

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

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a **crystal**. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure **3.3.3**. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

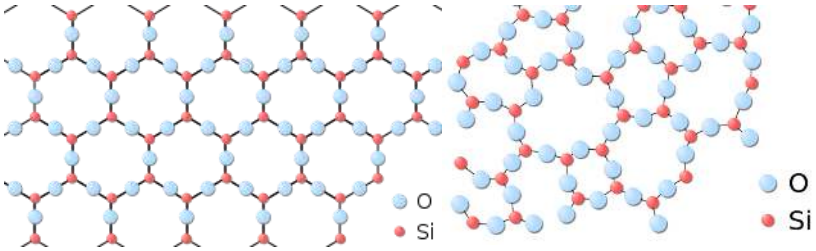


Figure **3.3.3**: (left) The periodic crystalline lattice structure of quartz SiO_2 in two-dimensions. (right) The random network structure of glassy SiO_2 in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in this plane. Images used with permission (public domain).

Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.

Liquids have the following characteristics:

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

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



Video* 3.3.1: Mercury boiling to become a gas.*

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

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. This describes the gas state, which we will consider in more detail elsewhere. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either. The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Gases have the following characteristics:

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

Table **3.3.1**: Characteristics of the Three States of Matter

Characteristics	Solids	Liquids	Gases
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

Example 3.3.1

What state or states of matter does each statement, describe?

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

Solution

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

Exercise 3.3.1

What state or states of matter does each statement describe?

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

Answer a:

solid

Answer b:

gas

Answer c:

solid

Summary

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

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3.4: Classifying Matter According to Its Composition

Learning Objectives

- Explain the difference between a pure substance and a mixture.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex to the simplest and most fundamental (Figure **3.4.1**). Matter can be classified into two broad categories: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning that it is the same everywhere) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**. Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

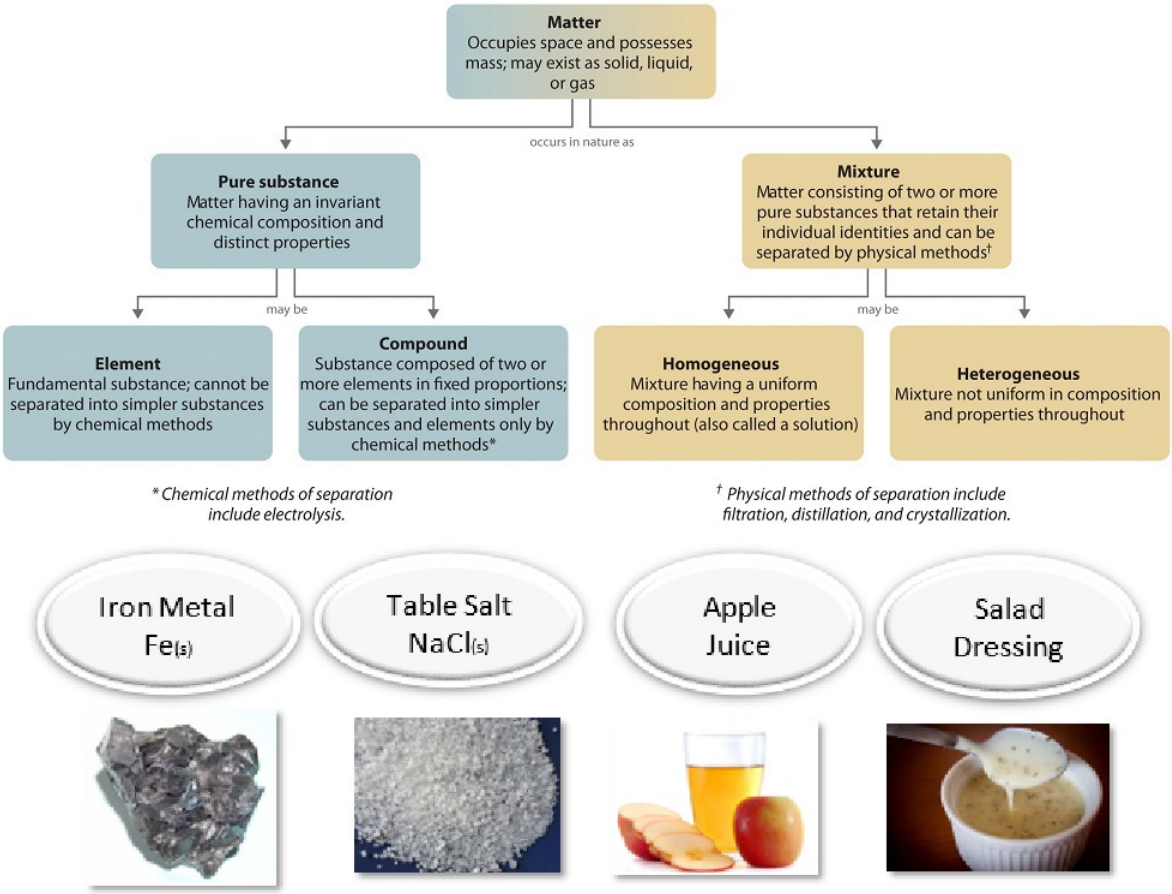


Figure **3.4.1**: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

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

properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

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

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

Phase

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

Example 3.4.1

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 3.4.1

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:
homogeneous mixture (solution)

Answer b:
element

Answer c:
heterogeneous mixture

Answer d:
compound

✔ Example 3.4.2

How would a chemist categorize each example of matter?

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

Solution

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of 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 3.4.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a:
a homogeneous mixture (solution), assuming it is filtered coffee

Answer b:
element

Answer c:
heterogeneous mixture

Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more

elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

Vocabulary

- Element: a substance that is made up of only one type of atom.
- Compound:a substance that is made up of more than one type of atom bonded together.
- Mixture: a combination of two or more elements or compounds which have not reacted to bond together; each part in the mixture retains its own properties.

Contributions & Attributions

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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3.5: Differences in Matter- Physical and Chemical Properties

Learning Objectives

To separate physical from chemical properties.

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

Physical Property

A *physical property* is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting point, and boiling point.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table **3.5.1**. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

Table **3.5.1**: Densities of Common Substances

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

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



Figure **3.5.1**: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

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

Chemical Properties

Chemical properties of matter describe its potential to undergo some chemical change or reaction by virtue of its composition. The elements, electrons, and bonds that are present give the matter potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually, after studying chemistry for some time, you should be able to look at the formula of a compound and state some chemical property. For example, hydrogen has the potential to ignite and explode given the right conditions—this is a chemical property. Metals in general have the chemical property of reacting with an acid. Zinc reacts with hydrochloric acid to produce hydrogen gas—this is a chemical property.



Figure **3.5.2**: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure **3.5.2**). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table **3.5.2**: Contrasting Physical and Chemical Properties

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

Example 3.5.1

Which of the following is a chemical property of iron?

a. Iron corrodes in moist air.
b. Density = 7.874 g/cm^3
c. Iron is soft when pure.
d. Iron melts at 1808 K.

Solution

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

Exercise 3.5.1A

Which of the following is a physical property of matter?

a. corrosiveness
b. pH (acidity)
c. density
d. flammability

Answer

c

Exercise 3.5.1B

Which of the following is a chemical property?

a. flammability
b. melting point
c. boiling point
d. density

Answer

a

Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

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3.6: Changes in Matter - Physical and Chemical Changes

Learning Objectives

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

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

Physical Change

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

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

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



Figure **3.6.1**: Ice melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; however, this change is only physical, as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

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

Chemical Change

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

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



Figure **3.6.2**: Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

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

Observations that help to indicate chemical change include:

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

✔ Example 3.6.1

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

a. Boiling water.
b. A nail rusting.
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution

a. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$

b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $Fe + O_2 \rightarrow Fe_2O_3$

c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.

d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

? Exercise 3.6.1

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

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer a:

physical change

Answer b:

chemical change

Answer c:

physical change

Answer d:

chemical change

Separating Mixtures Through Physical Changes

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.

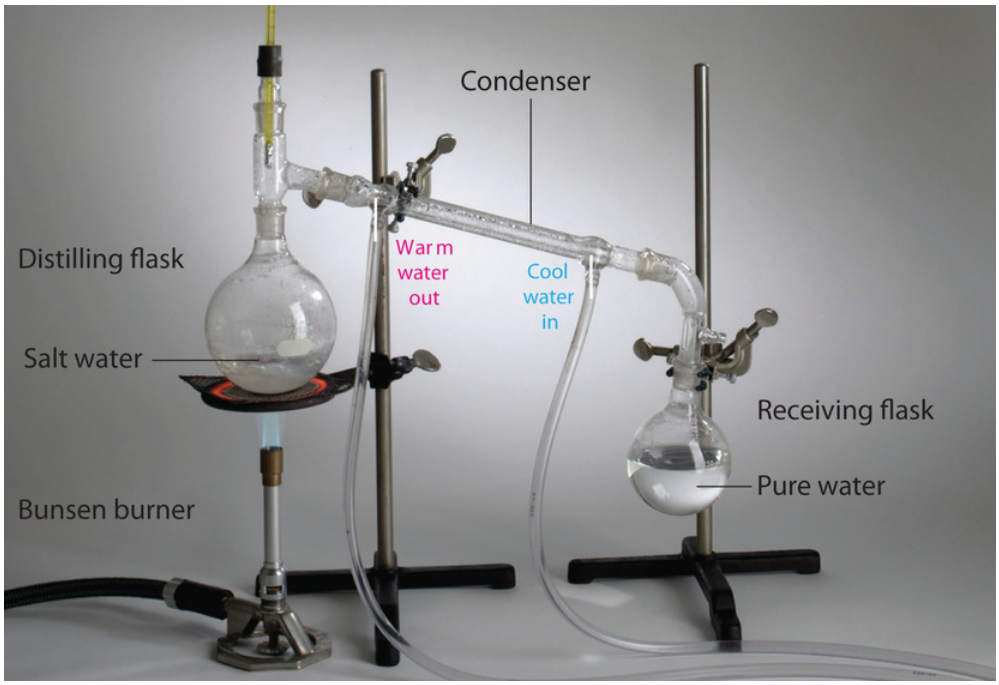


Figure **3.6.3***: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.*

Parts of a distillation setup: Bunsen burner, salt water in distilling flask, condenser with cool water in and warm water out, pure water in 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.

Another example for using physical properties to separate mixtures is filtration (Figure **3.6.4**). Filtration is any mechanical, physical or biological operation that separates solids from fluids (liquids or gases) by adding a medium through which only the fluid can pass. The fluid that passes through is called the filtrate. There are many different methods of filtration; all aim to attain the separation of substances. Separation is achieved by some form of interaction between the substance or objects to be removed and the filter. The substance that is to pass through the filter must be a fluid, i.e. a liquid or gas. Methods of filtration vary depending on the location of the targeted material, i.e. whether it is dissolved in the fluid phase or suspended as a solid.

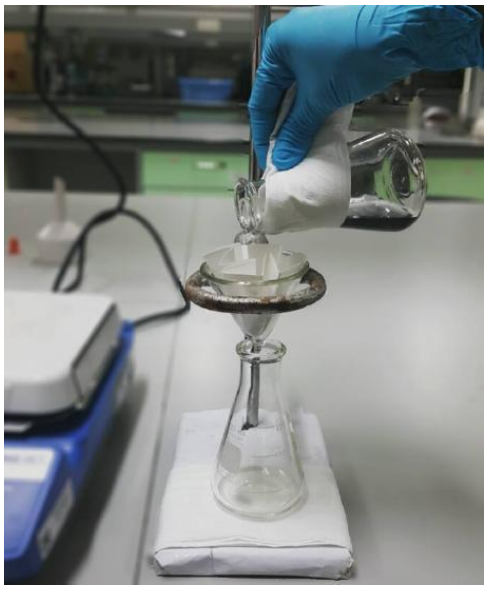


Figure **3.6.4***: Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

Summary

- Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change has occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

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3.7: Conservation of Mass - There is No New Matter

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Look at Figure **3.7.1** below. It shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose you had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose you had been able to measure the oxygen used by the fire and the gases produced by the fire. What would you find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

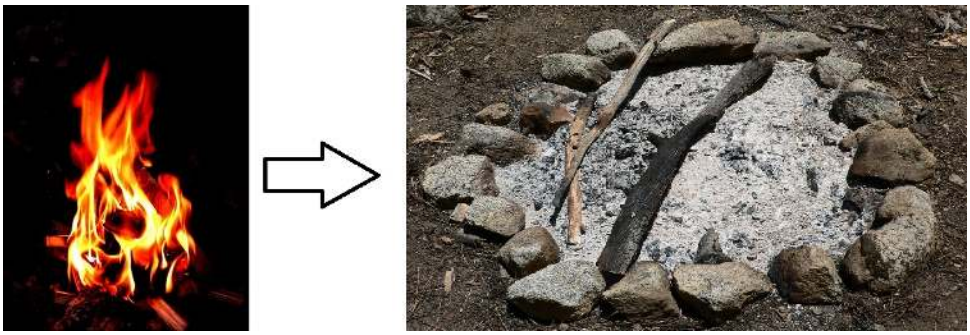


Figure **3.7.1**: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). (CC BY-SA 2.5; Einar Helland Berger for fire and Walter Siegmund for ash).

Law of Conservation of Mass

The law of conservation of mass was created in 1789 by a French chemist, Antoine Lavoisier. The **law of conservation of mass** states that matter cannot be created or destroyed in a chemical reaction. For example, when wood burns, the mass of the soot, ashes, and gases equals the original mass of the charcoal and the oxygen when it first reacted. So the mass of the product equals the mass of the reactant. A reactant is the chemical reaction of two or more elements to make a new substance, and a product is the substance that is formed as the result of a chemical reaction (Video **3.7.1**). Matter and its corresponding mass may not be able to be created or destroyed, but can change forms to other substances like liquids, gases, and solids.



Video **3.7.1**: This is a nice little demonstration showing the Conservation of Mass in action.

If you witness a 300 kg tree burn to the ground, there are only ashes left after the burn, and all of them together weigh 10 kg. It may make you wonder where the other 290 kg went. The missing 290 kg was released into the atmosphere as smoke, so the only thing left that you can see is the 10 kg of ash. If you know the law of conservation of mass, then you know that the other 290 kg has to go somewhere, because it has to equal the mass of the tree before it burnt down.

Example 3.7.1

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

Solution

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

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

Exercise 3.7.1

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

Answer

276.4 g of potassium carbonate

The Law is also applicable to both chemical and physical changes. For example, if you have an ice cube that melts into a liquid and you heat that liquid up, it becomes a gas. It will appear to have disappeared, but is still there.

Summary

- Burning and other changes in matter do not destroy matter.
- The mass of matter is always the same before and after the changes occur.
- The law of conservation of mass states that matter cannot be created or destroyed.

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3.8: Energy

Learning Objectives

- Define heat and work.
- Distinguish between kinetic energy and potential energy.
- State the law of conservation of matter and energy.

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

Ability to Do Work or Produce Heat

When we speak of *using* energy, we are really referring to *transferring* energy from one place to another. When you use energy to throw a ball, you transfer energy from your body to the ball, and this causes the ball to fly through the air. When you use energy to warm your house, you transfer energy from the furnace to the air in your home, and this causes the temperature in your house to rise. Although energy is used in many kinds of different situations, all of these uses rely on energy being transferred in one of two ways. Energy can be transferred as *heat* or as *work*.

When scientists speak of ***heat***, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature, as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot—the pot and the food inside the pot are cold. As a result, heat moves from the hot stove element to the cold pot. After a while, enough heat is transferred from the stove to the pot, raising the temperature of the pot and all of its contents (Figure **3.8.1**).



Figure **3.8.1**: Energy is transferred as heat from the hot stove element to the cooler pot until the pot and its contents become just as hot as the element. The energy that is transferred into the pot as heat is then used to cook the food.

Heat is only one way in which energy can be transferred. Energy can also be transferred as **work**. The scientific definition of work is *force (any push or pull) applied over a distance*. When you push an object and cause it to move, you do work, and you transfer some of *your* energy to the object. At this point, it's important to warn you of a common misconception. Sometimes we think that the amount of work done can be measured by the amount of effort put in. This may be true in everyday life, but it is not true in science. By definition, scientific work requires that force be applied *over a distance*. It does not matter how hard you push or how hard you pull. If you have not moved the object, you haven't done any work.

So far, we've talked about the two ways in which energy can be transferred from one place, or object, to another. Energy can be transferred as heat, and energy can be transferred as work. But the question still remains—*what IS energy*?

Kinetic Energy

Machines use energy, our bodies use energy, energy comes from the sun, energy comes from volcanoes, energy causes forest fires, and energy helps us to grow food. With all of these seemingly different types of energy, it's hard to believe that there are really only two different *forms* of energy: kinetic energy and potential energy. **Kinetic energy** is energy associated with motion. When an object is moving, it has kinetic energy. When the object stops moving, it has no kinetic energy. While all moving objects have kinetic energy, not all moving objects have the same amount of kinetic energy. The amount of kinetic energy possessed by an object is determined by its mass and its speed. The heavier an object is and the faster it is moving, the more kinetic energy it has.

Kinetic energy is very common, and it's easy to spot examples of it in the world around you. Sometimes we even try to capture kinetic energy and use it to power things like our home appliances. If you are from California, you might have driven through the Tehachapi Pass near Mojave or the Montezuma Hills in Solano County and seen the windmills lining the slopes of the mountains (Figure 3.8.2). These are two of the larger wind farms in North America. As wind rushes along the hills, the kinetic energy of the moving air particles turns the windmills, trapping the wind's kinetic energy so that people can use it in their houses and offices.



Figure 3.8.2: A wind farm in Solano County harnesses the kinetic energy of the wind. (CC BY-SA 3.0 Unported; BDS2006 at Wikipedia)

Potential Energy

Potential energy is *stored* energy. It is energy that remains available until we choose to use it. Think of a battery in a flashlight. If left on, the flashlight battery will run out of energy within a couple of hours, and the flashlight will die. If, however, you only use the flashlight when you need it, and turn it off when you don't, the battery will last for days or even months. The battery contains a certain amount of energy, and it will power the flashlight for a certain amount of time, but because the battery stores *potential* energy, you can choose to use the energy all at once, or you can save it and only use a small amount at a time.

Any stored energy is potential energy. There are a lot of different ways in which energy can be stored, and this can make potential energy very difficult to recognize. In general, an object has potential energy because of its *position relative to another object*. For example, when a rock is held above the earth, it has potential energy because of its position relative to the ground. This is *potential energy* because the energy is *stored* for as long as the rock is held in the air. Once the rock is dropped, though, the stored energy is released as kinetic energy as the rock falls.

Chemical Energy

There are other common examples of potential energy. A ball at the top of a hill stores potential energy until it is allowed to roll to the bottom. When two magnets are held next to one another, they store potential energy too. For some examples of potential energy, though, it's harder to see how "position" is involved. In chemistry, we are often interested in what is called **chemical potential energy**. Chemical potential energy is energy stored in the atoms, molecules, and chemical bonds that make up matter. How does this depend on position?

As you learned earlier, the world, and all of the chemicals in it are made up of atoms and molecules. These store potential energy that is dependent on their positions relative to one another. Of course, you can't see atoms and molecules. Nevertheless, scientists do know a lot about the ways in which atoms and molecules interact, and this allows them to figure out how much potential energy

is stored in a specific quantity (like a cup or a gallon) of a particular chemical. *Different chemicals have different amounts of potential energy* because they are made up of different atoms, and those atoms have different positions relative to one another.

> Since different chemicals have different amounts of potential energy, scientists will sometimes say that potential energy depends not only on ***position***, but also on ***composition***. Composition affects potential energy because it determines which molecules and atoms end up next to one another. For example, the total potential energy in a cup of pure water is different than the total potential energy in a cup of apple juice, because the cup of water and the cup of apple juice are *composed* of different amounts of different chemicals.

At this point, you may wonder just how useful chemical potential energy is. If you want to release the potential energy stored in an object held above the ground, you just drop it. But how do you get potential energy out of chemicals? It's actually not difficult. Use the fact that different chemicals have *different amounts of potential energy*. If you start with chemicals that have a lot of potential energy and allow them to react and form chemicals with less potential energy, all the extra energy that was in the chemicals at the beginning, but not at the end, is released.

Units of Energy

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

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

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

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

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

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

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

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

Summary

- Any time we use energy, we transfer energy from one object to another.
- Energy can be transferred in one of two ways: as heat, or as work.
- Heat is the term given to energy that is transferred from a hot object to a cooler object due to the difference in their temperatures.
- Work is the term given to energy that is transferred as a result of a force applied over a distance.
- Energy comes in two fundamentally different forms: kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.
- Chemical potential energy is a special type of potential energy that depends on the positions of different atoms and molecules relative to one another.
- Chemical potential energy can also be thought of according to its dependence on chemical composition.
- Energy can be converted from one form to another. The total amount of mass and energy in the universe is conserved.

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3.9: Energy and Chemical and Physical Change

Learning Objectives

- Define endothermic and exothermic reactions.
- Describe how heat is transferred in endothermic and exothermic reactions.
- Determine whether a reaction is endothermic or exothermic through observations, temperature changes, or an energy diagram.

So far, we have talked about how energy exists as either *kinetic energy* or *potential energy* and how energy can be transferred as either *heat* or *work*. While it's important to understand the difference between kinetic energy and potential energy and the difference between heat and work, the truth is, energy is constantly changing. Kinetic energy is constantly being turned into potential energy, and potential energy is constantly being turned into kinetic energy. Likewise, energy that is transferred as work might later end up transferred as heat, while energy that is transferred as heat might later end up being used to do work.

Even though energy can change form, it must still follow one fundamental law: *Energy cannot be created or destroyed, it can only be changed from one form to another*. This law is known as the **Law of Conservation of Energy**. In a lot of ways, energy is like money. You can exchange quarters for dollar bills and dollar bills for quarters, but no matter how often you convert between the two, you will not end up with any more or any less money than you started with. Similarly, you can transfer (or spend) money using cash, or transfer money using a credit card; but you still spend the same amount of money, and the store still makes the same amount of money.

A campfire is an example of basic thermochemistry. The reaction is initiated by the application of heat from a match. The reaction converting wood to carbon dioxide and water (among other things) continues, releasing heat energy in the process. This heat energy can then be used to cook food, roast marshmallows, or just keep warm when it's cold outside.



An image of a campfire with colored flames, made by the burning of a garden hose in a copper pipe. (CC SA-BY 3.0; Jared)

Exothermic and Endothermic Processes

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe: *the system* and *the surroundings*. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** are everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings are the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter q. The sign of q for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings are gaining heat from the system, the temperature of the surroundings increases. The sign of q for an exothermic process is negative because the system is losing heat.

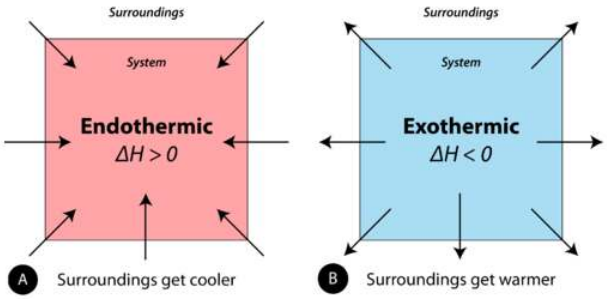


Figure 3.9.1: (A) Endothermic reaction. (B) Exothermic reaction.

Endothermic reaction: surroundings get cooler and delta H is greater than 0, Exothermic reaction: surroundings get warmer and delta H is less than 0

During phase changes, energy changes are usually involved. For example, when solid dry ice vaporizes (physical change), carbon dioxide molecules absorb energy. When liquid water becomes ice, energy is released. Remember that all chemical reactions involve a change in the bonds of the reactants. The bonds in the reactants are broken and the bonds of the products are formed. Chemical bonds have **potential energy** or "stored energy". Because we are changing the bonding, this means we are also changing how much of this "stored energy" there is in a reaction.

Energy changes are frequently shown by drawing an energy diagram. Energy diagrams show the stored/hidden energy of the reactants and products as well as the activation energy. If, on an energy diagram, the products have more stored energy than the reactants started with, the reaction is endothermic. You had to give the reaction energy. If, on the energy diagram, the products have less stored energy than the reactants started with, the reaction is exothermic.

✔ Example 3.9.1

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. gasoline burning
c. ice forming on a pond

Solution

a. Endothermic—you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
b. Exothermic—when you burn something, it feels hot to you because it is giving off heat into the surroundings.
c. Exothermic—think of ice forming in your freezer instead. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

? Exercise 3.9.1

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

Answer (a)

exothermic

Answer (b)

endothermic

Summary

Phase changes involve changes in energy. All chemical reactions involve changes in energy. This may be a change in heat, electricity, light, or other forms of energy. Reactions that absorb energy are endothermic. Reactions that release energy are exothermic.

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3.10: Temperature - Random Motion of Molecules and Atoms

Learning Objectives

- Identify the different between temperature and heat.
- Recognize the different scales used to measure temperature

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. Temperature is a measure of the average kinetic energy of the particles in matter. In everyday usage, temperature indicates a measure of how hot or cold an object is. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there was in increase in the temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at lower temperatures.



Figure **3.10.1**: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

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



Figure **3.10.2**: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right).

The Fahrenheit Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale was first developed in 1724 and tinkered with for some time after that. The main problem with this scale is the arbitrary definitions of temperature. The freezing point of water was defined as $32°F$ and the boiling point as $212°F$. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Scale

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

The Kelvin Scale

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

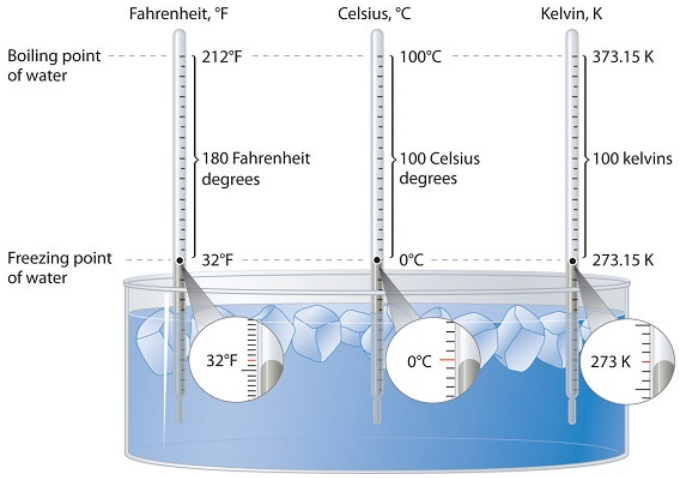


Figure 3.10.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

Converting Between Scales

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

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

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

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

$$°C = \frac{(°F - 32)}{1.8} \tag{3.10.3}$$

$$°F = 1.8 \times (°C) + 32 \tag{3.10.4}$$

Example 3.10.1: Temperature Conversions

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

Solution

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

$$°C = \frac{(103.5°F - 32)}{1.8} \tag{3.10.1}$$

$$= 39.7\,°C \tag{3.10.2}$$

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

$$K = 39.7\,°C + 273.15 \tag{3.10.3}$$
$$= 312.9\,K \tag{3.10.4}$$

Exercise 3.10.1

Convert each temperature to °C and °F.

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

Answer (a)

5527 K, 9980 °F

Answer (b)

2807 K, 5084 °F

Answer (c)

-195.79 K, -320.42 °F

Summary

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K).

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CHAPTER OVERVIEW

4: Atoms, Elements, and the Periodic Table

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- 4.1: Cutting Aluminum until you get Atoms
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- 4.3: The Nuclear Atom
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- 4.5: The Electromagnetic Spectrum
- 4.6: The Bohr Model - Atoms with Orbits
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- 4.8: Mendeleev and Periodic Table
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- 4.11: Quantum-Mechanical Orbitals and Electron Configurations
- 4.12: Electron Configurations and the Periodic Table
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4.1: Cutting Aluminum until you get Atoms

Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC by Democritus and other ancient Greek philosophers (Figure **4.1.1**).

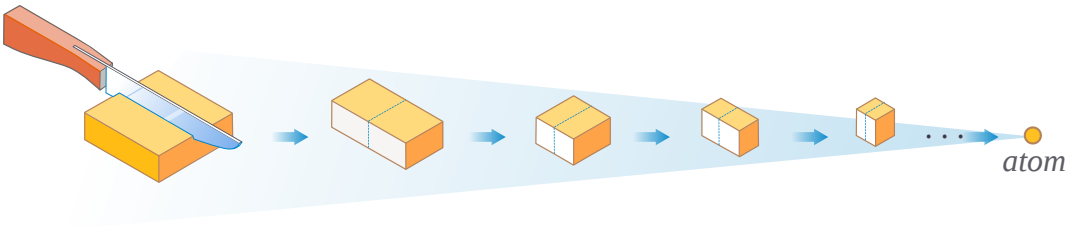


Figure **4.1.1**: Democritus argued that matter, like an aluminum block, cannot be repeatedly cut in half perpetually. At some point, a limit is reached before the substance can no longer be called "aluminum"; this is the atomic limit. (CC BY-NC; Ümit Kaya via LibreTexts)

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called diatomic molecules. In representing a diatomic molecule, we use the symbol of the element and include the subscript 2 to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

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4.2: 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 **4.2.1**: (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.

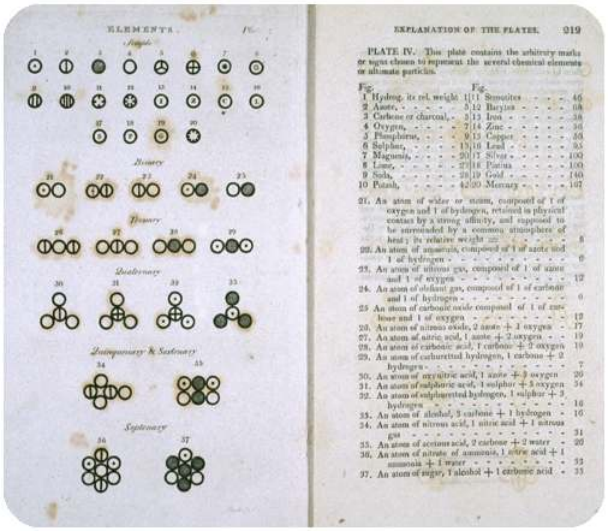
The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **4.2.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

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 **4.2.2**: 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 **4.2.1**, control of individual atoms can be use used create animations.



Video **4.2.1**: 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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4.3: The Nuclear Atom

Learning Objectives

- Explain the observations that led to Thomson's discovery of the electron.
- Describe Thomson's "plum pudding" model of the atom and the evidence for it.
- Draw a diagram of Thomson's "plum pudding" model of the atom and explain why it has this name.
- Describe Rutherford's gold foil experiment and explain how this experiment altered the "plum pudding" model.
- Draw a diagram of the Rutherford model of the atom and label the nucleus and the electron cloud.

Dalton's Atomic Theory held up well to a lot of the different chemical experiments that scientists performed to test it. In fact, for almost 100 years, it seemed as if Dalton's Atomic Theory was the whole truth. However, in 1897, a scientist named J. J. Thomson conducted some research that suggested that Dalton's Atomic Theory was not the entire story. He suggested that the small, negatively charged particles making up the cathode ray were actually pieces of atoms. He called these pieces "corpuscles," although today we know them as **electrons**. Thanks to his clever experiments and careful reasoning, J. J. Thomson is credited with the discovery of the electron.



Figure **4.3.1**: J. J. Thomson (center) concluded experiments that suggested that Dalton's (left) atomic theory was not telling the entire story. Ernest Rutherford (right) later built on Thomson's work to argue for the model nuclear atom.

Electrons and Plums

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

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

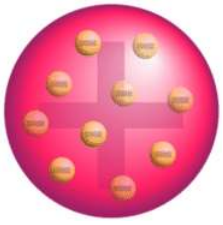


Figure **4.3.2**: The "plum pudding" model.

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

Atoms and Gold

In 1911, Rutherford and coworkers Hans Geiger and Ernest Marsden initiated a series of groundbreaking experiments that would completely change the accepted model of the atom. They bombarded very thin sheets of gold foil with fast moving **alpha particles**. Alpha particles, a type of natural radioactive particle, are positively charged particles with a mass about four times that of a hydrogen atom.

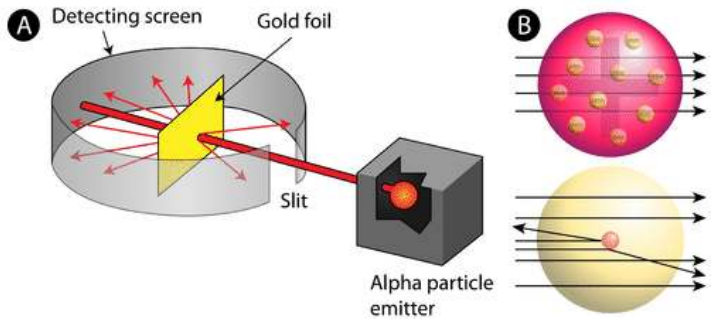


Figure **4.3.3**: (A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding model (top), all of the alpha particles should have passed through the gold foil with little or no deflection. Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

According to the accepted atomic model, in which an atom's mass and charge are uniformly distributed throughout the atom, the scientists expected that all of the alpha particles would pass through the gold foil with only a slight deflection or none at all. Surprisingly, while most of the alpha particles were indeed not deflected, a very small percentage (about 1 in 8000 particles) bounced off the gold foil at very large angles. Some were even redirected back toward the source. No prior knowledge had prepared them for this discovery. In a famous quote, Rutherford exclaimed that it was "as if you had fired a 15-inch [artillery] shell at a piece of tissue and it came back and hit you."

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

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

Rutherford's model proved to be an important step towards a full understanding of the atom. However, it did not completely address the nature of the electrons and the way in which they occupy the vast space around the nucleus. It was not until some years later that a full understanding of the electron was achieved. This proved to be the key to understanding the chemical properties of elements.

Atomic Nucleus

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

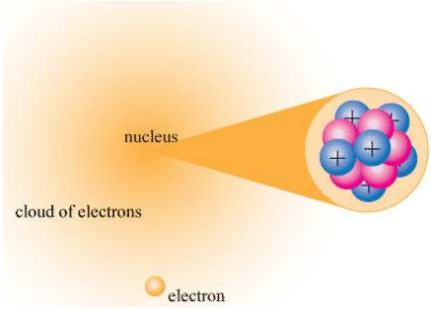


Figure **4.3.4**: The nuclear atom.

The nucleus of the atom is extremely small. Its radius is only about 1/100,000 of the total radius of the atom. Electrons have virtually no mass, but protons and neutrons have a lot of mass for their size. As a result, the nucleus has virtually all the mass of an atom. Given its great mass and tiny size, the nucleus is very dense. If an object the size of a penny had the same density as the nucleus of an atom, its mass would be greater than 30 million tons!

Holding it all Together

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

Summary

- Atoms are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of atoms and how they compose matter.
- Bombardment of gold foil with alpha particles showed that some particles were deflected.
- The nuclear model of the atom consists of a small and dense positively charged interior surrounded by a cloud of electrons.

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4.4: The Properties of Protons, Neutrons, and Electrons

Learning Objectives

- Describe the locations, charges, and masses of the three main subatomic particles.
- Determine the number of protons and electrons in an atom.
- Define atomic mass unit (amu).

Dalton's Atomic Theory explained a lot about matter, chemicals, and chemical reactions. Nevertheless, it was not entirely accurate, because contrary to what Dalton believed, atoms can, in fact, be broken apart into smaller subunits or subatomic particles. We have been talking about the electron in great detail, but there are two other particles of interest to us: protons and neutrons. We already learned that J. J. Thomson discovered a negatively charged particle, called the **electron**. Rutherford proposed that these electrons orbit a positive nucleus. In subsequent experiments, he found that there is a smaller positively charged particle in the nucleus, called a **proton**. There is also a third subatomic particle, known as a neutron.

Electrons

Electrons are one of three main types of particles that make up atoms. Unlike protons and neutrons, which consist of smaller, simpler particles, electrons are fundamental particles that do not consist of smaller particles. They are a type of fundamental particle called leptons. All leptons have an electric charge of -1 or 0. Electrons are extremely small. The mass of an electron is only about 1/2000 the mass of a proton or neutron, so electrons contribute virtually nothing to the total mass of an atom. Electrons have an electric charge of -1, which is equal but opposite to the charge of a proton, which is $+1$. All atoms have the same number of electrons as protons, so the positive and negative charges "cancel out", making atoms electrically neutral.

Unlike protons and neutrons, which are located inside the nucleus at the center of the atom, electrons are found outside the nucleus. Because opposite electric charges attract one another, negative electrons are attracted to the positive nucleus. This force of attraction keeps electrons constantly moving through the otherwise empty space around the nucleus. The figure below is a common way to represent the structure of an atom. It shows the electron as a particle orbiting the nucleus, similar to the way that planets orbit the sun. However, this is an incorrect perspective, as quantum mechanics demonstrates that electrons are more complicated.



Figure 4.4.1: Electrons are much smaller than protons or neutrons. If an electron was the mass of a penny, a proton or a neutron would have the mass of a large bowling ball!

Protons

A proton is one of three main particles that make up the atom. Protons are found in the nucleus of the atom. This is a tiny, dense region at the center of the atom. Protons have a positive electrical charge of one $(+1)$ and a mass of 1 atomic mass unit (amu), which is about 1.67×10^{-27} kilograms. Together with neutrons, they make up virtually all of the mass of an atom.

Neutrons

Atoms of all elements—except for most atoms of hydrogen—have neutrons in their nucleus. Unlike protons and electrons, which are electrically charged, neutrons have no charge—they are electrically neutral. That's why the neutrons in the diagram above are labeled n^0. The zero stands for "zero charge". The mass of a neutron is slightly greater than the mass of a proton, which is 1 atomic

mass unit (amu). (An atomic mass unit equals about 1.67×10^{-27} kilograms.) A neutron also has about the same diameter as a proton, or 1.7×10^{-15} meters.

As you might have already guessed from its name, the neutron is neutral. In other words, it has no charge whatsoever and is therefore neither attracted to nor repelled from other objects. Neutrons are in every atom (with one exception), and they are bound together with other neutrons and protons in the atomic nucleus.

Before we move on, we must discuss how the different types of subatomic particles interact with each other. When it comes to neutrons, the answer is obvious. Since neutrons are neither attracted to nor repelled from objects, they don't really interact with protons or electrons (beyond being bound into the nucleus with the protons).

Even though electrons, protons, and neutrons are all types of subatomic particles, they are not all the same size. When you compare the masses of electrons, protons, and neutrons, what you find is that electrons have an extremely small mass, compared to either protons or neutrons. On the other hand, the masses of protons and neutrons are fairly similar, although technically, the mass of a neutron is slightly larger than the mass of a proton. Because protons and neutrons are so much more massive than electrons, almost all of the mass of any atom comes from the nucleus, which contains all of the neutrons and protons.

Table 4.4.1: Properties of Subatomic Particles

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

Table 4.4.1 gives the properties and locations of electrons, protons, and neutrons. The third column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (amu)** is defined as one-twelfth of the mass of a carbon-12 atom. Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1 in this unit system.

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

Summary

- Electrons are a type of subatomic particle with a negative charge.
- Protons are a type of subatomic particle with a positive charge. Protons are bound together in an atom's nucleus as a result of the strong nuclear force.
- Neutrons are a type of subatomic particle with no charge (they are neutral). Like protons, neutrons are bound into the atom's nucleus as a result of the strong nuclear force.
- Protons and neutrons have approximately the same mass, but they are both much more massive than electrons (approximately 2,000 times as massive as an electron).
- The positive charge on a proton is equal in magnitude to the negative charge on an electron. As a result, a neutral atom must have an equal number of protons and electrons.
- The atomic mass unit (amu) is a unit of mass equal to one-twelfth the mass of a carbon-12 atom

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4.5: The Electromagnetic Spectrum

Learning Objectives

- Know the properties of different types of electromagnetic radiation.

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

The figure below shows the **electromagnetic spectrum**, which is all forms of electromagnetic radiation. On the far left of Figure **4.5.1** are the highest energy electromagnetic waves. These are called **gamma rays** and can be quite dangerous, in large numbers, to living systems. The next lower energy form of electromagnetic waves are called **x-rays**. Most of you are familiar with the penetration abilities of these waves. They can also be dangerous to living systems. Humans are advised to limit as much as possible the number of medical x-rays they have per year. Next lower, in energy, are **ultraviolet rays**. These rays are part of sunlight and the upper end of the ultraviolet range can cause sunburn and perhaps skin cancer. The tiny section next in the spectrum is the **visible range of light**. The visible light spectrum has been greatly expanded in the bottom half of the figure so that it can be discussed in more detail. The visible range of electromagnetic radiation are the frequencies to which the human eye responds. Lower in the spectrum are infrared rays and radio waves.

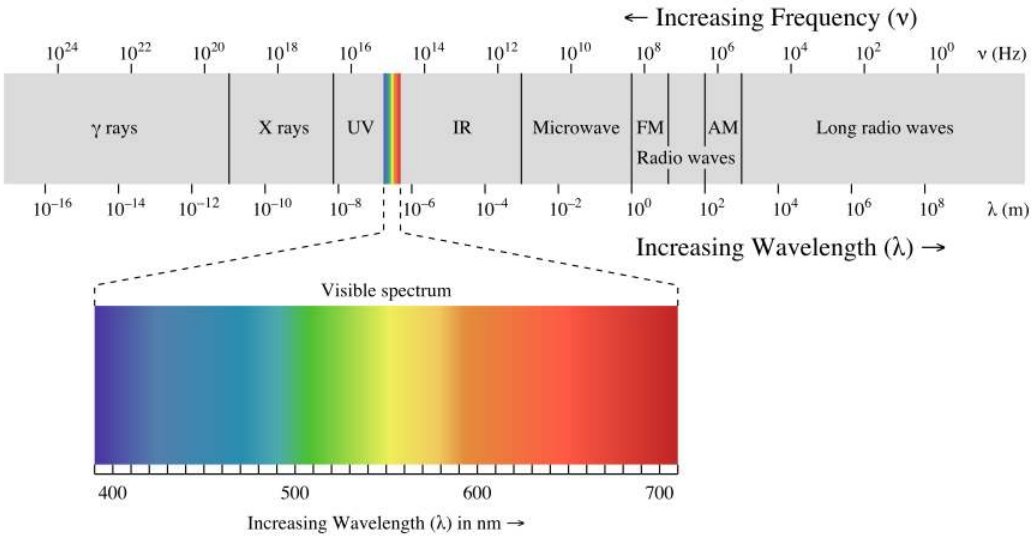


Figure **4.5.1**: The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate. (CC BY-NC-SA; anonymous by request).

The light energies that are in the visible range are electromagnetic waves that cause the human eye to respond when those frequencies enter the eye. The eye sends a signal to the brain and the individual "sees" various colors. The highest energy waves in the visible region cause the brain to see violet and as the energy decreases, the colors change to blue, green, yellow, orange, and red. When the energy of the wave is above or below the visible range, the eye does not respond to them. When the eye receives several different frequencies at the same time, the colors are blended by the brain. If all frequencies of light strike the eye together, the brain sees white. If there are no visible frequencies striking the eye, the brain sees black. The objects that you see around you are light absorbers—that is, the chemicals on the surface of the object will absorb certain frequencies and not others. Your eyes detect the frequencies that strike your eye. Therefore, if your friend is wearing a red shirt, it means the dye in that shirt absorbs every frequency except red and the red frequencies are reflected. If your only light source was one exact frequency of blue light and you shined it on a shirt that was red in sunlight, the shirt would appear black because no light would be reflected. The light from fluorescent types of lights do not contain all the frequencies of sunlight and so clothes inside a store may appear to be a slightly different color when you get them home.

Summary

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

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4.6: The Bohr Model - Atoms with Orbits

Learning Objectives

- Define an energy level in terms of the Bohr model.
- Discuss how the Bohr model can be used to explain atomic spectra.

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



Figure 4.6.1: Human/Need/Desire. Neon sculpture by Bruce Nauman (1983), who has been characterized as a conceptual artist.

Each Element Has a Unique Spectrum

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



Figure 4.6.2: Atomic Emission Spectrum of Hydrogen.

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

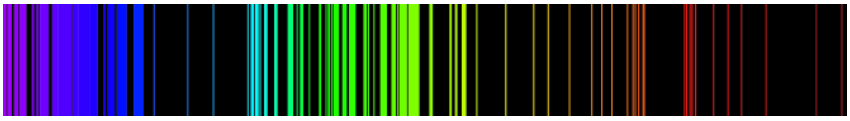


Figure 4.6.3: Atomic Emission Spectrum of Iron.

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

Bohr's Model of the Atom

By 1913, the concept of the atom had evolved from Dalton's indivisible spheres idea, to J. J. Thomson's plum pudding model, and then to Rutherford's nuclear atom theory. Rutherford, in addition to carrying out the brilliant experiment that demonstrated the presence of the atomic nucleus, also proposed that the electrons circled the nucleus in a planetary type motion. The solar system or 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.



Figure **4.6.3**: Niels Bohr with Albert Einstein at Paul Ehrenfest's home in Leiden (December 1925).

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. Furthermore, Rutherford's model was unable to describe how electrons give off light forming each element's unique atomic spectrum. These difficulties cast a shadow on the planetary model and indicated that, eventually, it would have to be replaced.

In 1913, the Danish physicist Niels Bohr proposed a model of the electron cloud of an atom in which electrons orbit the nucleus and were able to produce atomic spectra. Understanding Bohr's model requires some knowledge of electromagnetic radiation (or light).

Energy Levels

Bohr's key idea in his model of the atom is that electrons occupy definite orbitals that require the electron to have a specific amount of energy. In order for an electron to be in the electron cloud of an atom, it must be in one of the allowable orbitals and it must have the precise energy required for that orbit. Orbits closer to the nucleus would require smaller amounts of energy for an electron, and orbits farther from the nucleus would require the electron to have a greater amount of energy. The possible orbits are known as **energy levels**. One of the weaknesses of Bohr's model was that he could not offer a reason why only certain energy levels or orbits were allowed.

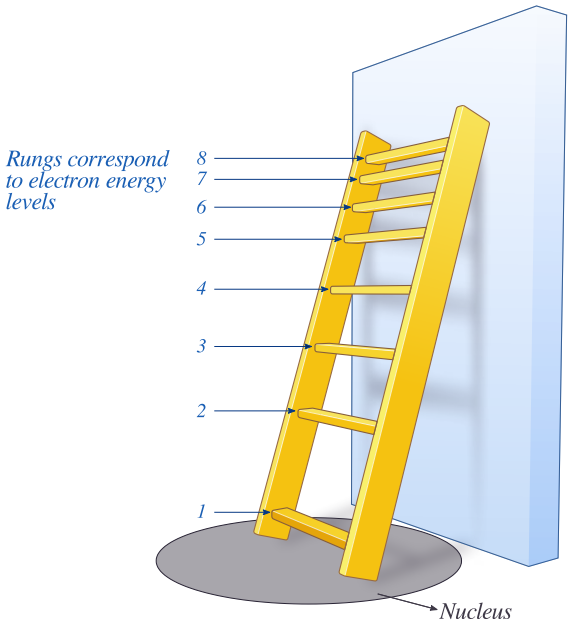


Figure **4.6.4**: The energy levels of the electrons can be viewed as rungs on a ladder. Note that the spacing between rungs gets smaller at higher energies (CC BY-NC; Ümit Kaya)

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

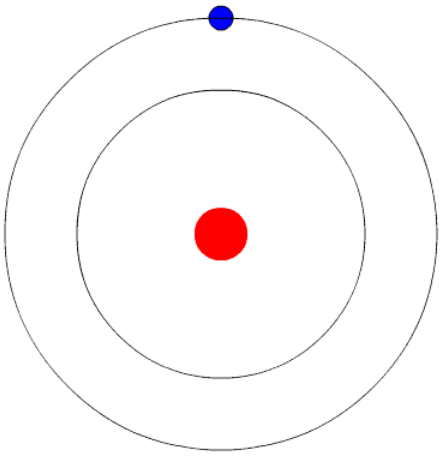


Figure **4.6.5**: In Bohr's Model of the atom, electrons absorb energy to move to a higher level and release energy to move to lower levels. (CC BY-SA 3.0; Kurzon).

Bohr's Model and Atomic Spectra

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

Summary

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

Vocabulary

- **Emission spectrum** (or **atomic spectrum**) - The unique pattern of light given off by an element when it is given energy.
- **Energy levels** - Possible orbits that an electron can have in the electron cloud of an atom.
- **Ground state** - To be in the lowest energy level possible.
- **Excited state** - To be in a higher energy level.
- **Photon** - A piece of electromagnetic radiation, or light, with a specific amount of energy.
- **Quantized** - To have a specific amount.

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4.7: Elements- Defined by Their Number of Protons

Learning Objectives

- Define atomic number.
- Define mass number.
- Determine the number of protons, neutrons, and electrons in an atom.

It's important to be able to distinguish atoms of one element from atoms of another element. Elements are pure substances that make up all other matter, so each one is given a unique name. The names of elements are also represented by unique one- or two-letter symbols, such as **H** for hydrogen, **C** for carbon, or **He** for helium. However, it would more powerful if these names could be used to identify the numbers of protons and neutrons in the atoms. That's where atomic number and mass number are useful.



Figure **4.7.1**: It is difficult to find qualities that differ between each element, and to distinguish one element from another. Each element, however, does have a unique number of protons. Sulfur has 16 protons, silicon has 14 protons, and gold has 79 protons. Images used with permission (public domain for sulfur and silicon, gold is licensed by CC-BY-SA-NC-ND; Alchemist-hp).

Atomic Number

Scientists distinguish between different elements by counting the number of protons in the nucleus (Table **4.7.1**). If an atom has only one proton, we know that it's a hydrogen atom. An atom with two protons is always a helium atom. If scientists count four protons in an atom, they know it's a beryllium atom. An atom with three protons is a lithium atom, an atom with five protons is a boron atom, an atom with six protons is a carbon atom . . . the list goes on.

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

Table **4.7.1**: Atoms of the First Six Elements

Name	Protons	Neutrons	Electrons	Atomic Number (Z)	Mass Number (A)
Hydrogen	1	0	1	1	1
Helium	2	2	2	2	4
Lithium	3	4	3	3	7
Beryllium	4	5	4	4	9
Boron	5	6	5	5	11
Carbon	6	6	6	6	12

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

Neutral Atoms

Atoms are neutral in electrical charge because they have the same number of negative electrons as positive protons (Table 4.7.1). Therefore, the atomic number of an atom also tells you how many electrons the atom has. This, in turn, determines many of the atom's chemical properties.

Mass Number

The **mass number** (A) of an atom is the total number of protons and neutrons in its nucleus. The mass of the atom is a unit called the atomic mass unit (amu). One atomic mass unit is the mass of a proton, or about 1.67×10^{-27} kilograms, which is an extremely small mass. A neutron has just a tiny bit more mass than a proton, but its mass is often assumed to be one atomic mass unit as well. Because electrons have virtually no mass, just about all the mass of an atom is in its protons and neutrons. Therefore, the total number of protons and neutrons in an atom determines its mass in atomic mass units (Table 4.7.1).

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

Why do you think that the "mass number" includes protons and neutrons, but not electrons? You know that most of the mass of an atom is concentrated in its nucleus. The mass of an atom depends on the number of protons and neutrons. You have already learned that the mass of an electron is very, very small compared to the mass of either a proton or a neutron (like the mass of a penny compared to the mass of a bowling ball). Counting the number of protons and neutrons tells scientists about the total mass of an atom.

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

An atom's mass number is very easy to calculate, provided that you know the number of protons and neutrons in an atom.

Example 4.5.1

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

Solution

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

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

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

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

A **chemical symbol** is a one- or two-letter designation of an element. Some examples of chemical symbols are **O** for oxygen, **Zn** for zinc, and **Fe** for iron. The first letter of a symbol is always capitalized. If the symbol contains two letters, the second letter is lower case. The majority of elements have symbols that are based on their English names. However, some of the elements that have been known since ancient times have maintained symbols that are based on their Latin names, as shown in Table 4.7.2.

Table 4.7.2: *Symbols and Latin Names for Elements*

Chemical Symbol	Name	Latin Name
Na	Sodium	Natrium
K	Potassium	Kalium
Fe	Iron	Ferrum
Cu	Copper	Cuprum
Ag	Silver	Argentum
Sn	Tin	Stannum
Sb	Antimony	Stibium
Au	Gold	Aurum
Pb	Lead	Plumbum

Summary

- Elements are pure substances that make up all matter, so each one is given a unique name.
- The names of elements are also represented by unique one- or two-letter symbols.
- Each element has a unique number of protons. An element's atomic number is equal to the number of protons in the nuclei of any of its atoms.
- The mass number of an atom is the sum of the protons and neutrons in the atom.
- Isotopes are atoms of the same element (same number of protons) that have different numbers of neutrons in their atomic nuclei.

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4.8: Mendeleev and Periodic Table

Learning Objectives

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

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

Emerging Patterns and Periodicity within the Known Elements

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

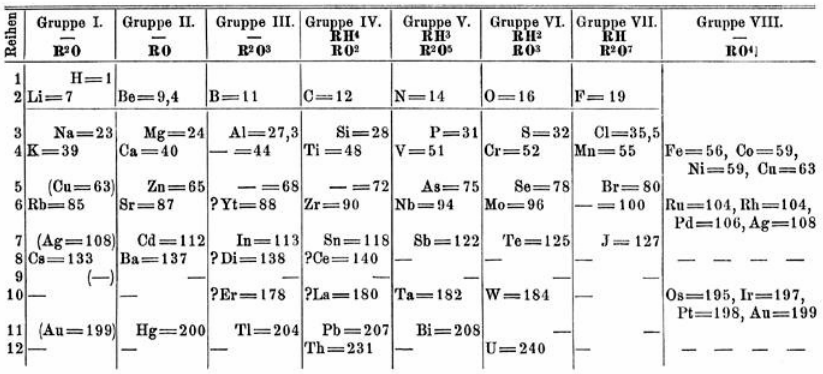
By the mid-19th century, the atomic masses of many of the elements had been determined. Scientists like John Newlands and Alexandre-Emile Béguyer de Chancourtois formed their own versions of periodic tables. The English chemist John Newlands (1838–1898), who hypothesized that the chemistry of the elements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

The Periodic Table: Mendeleev and Meyer

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

$$\frac{molar\ mass\ \left(g/mol\right)}{density\ \left(g/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{3.1.1}$$

Mendeleev, who first published his periodic table in 1869 (Figure **4.8.1**), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements, and that of Meyer and others, is that Mendeleev did not assume that all the elements had been discovered (in fact, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100—in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.



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

Figure 4.8.1: **Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in 1872.** The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

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

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 4.8.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.



Video 4.8.1: The genius of Mendeleev's periodic table.

Table 4.8.1: Comparison of the Properties Predicted by Mendeleev in 1869 for *eka*-Aluminum and *eka*-Silicon with the Properties of Gallium (discovered in 1875) and Germanium (discovered in 1886).

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	d = 5.9 g/cm^3	d = 5.91 g/cm^3	d = 5.5 g/cm^3	d = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	d = 5.5 g/cm^3	d = 6.0 g/cm^3	d = 4.7 g/cm^3	d = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C

*mp = melting point; bp = boiling point.

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

One group of elements that was absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later—between 1894 and 1898—by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium; so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals. In 1913, however, young British physicist H. G. J. Moseley (1887–1915) analyzed the frequencies of x-rays emitted by the elements, and discovered that the underlying foundation of the order of the elements was by the *atomic number*—not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z, which is the number of positive charges (protons) in its nucleus. Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey. Finally, in 1945, the Manhattan Project yielded the discovery of many new radioactive elements. Glenn T. Seaborg suggested an addition of the actinide and lanthanide series at the bottom of the table. This idea came with the discovery of Americium and Curium, and their unique properties. The change was not accepted at first, but is now included in all periodic tables. Figure **4.8.2** shows the time period for the discovery of the different elements.

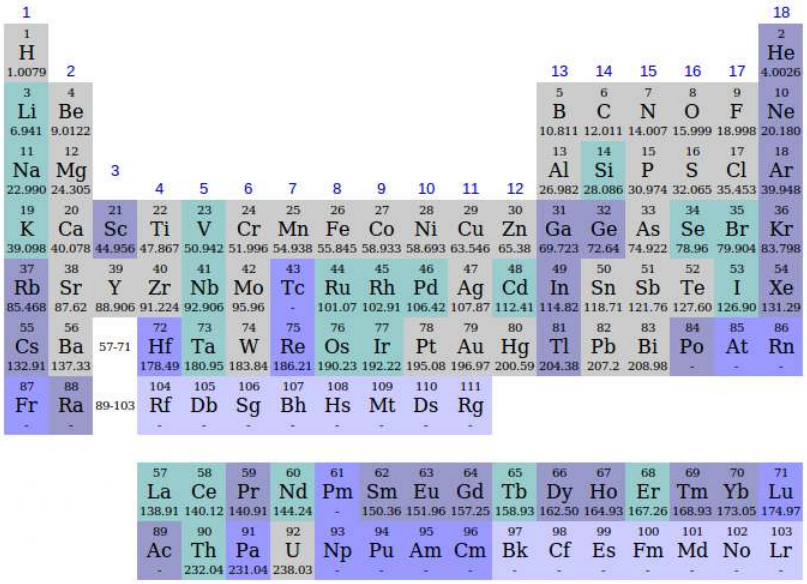


Figure **4.8.2** *Periodic table showing when each element was discovered*

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

Each element on the modern periodic table is represented by its atomic number and atomic mass (Figure **4.8.3**). The **atomic mass** of each element is found under the element symbol in the **periodic table.** Examples are shown below. The atomic mass of tin (Sn) is 118.71 u while the atomic mass of carbon (C) is 12.011 u. On the other hand, the **atomic number (Z)** of each element is found **above** the atomic symbol.

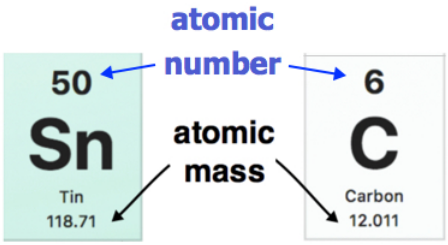


Figure **4.8.3**: Key information of an element indicated on entries of the Periodic Table. (public Domain; Pubchem)

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

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

Summary

- The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties.
- The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, both of whom focused on the relationship between atomic mass and chemical properties.
- The correlation with the electronic structure of atoms was discovered when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

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4.9: Looking for Patterns - The Periodic Table

Learning Objectives

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

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

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

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

The periodic table is one of the cornerstones of chemistry because it organizes all of the known elements on the basis of their chemical properties. A modern version is shown in Figure **4.9.1**. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

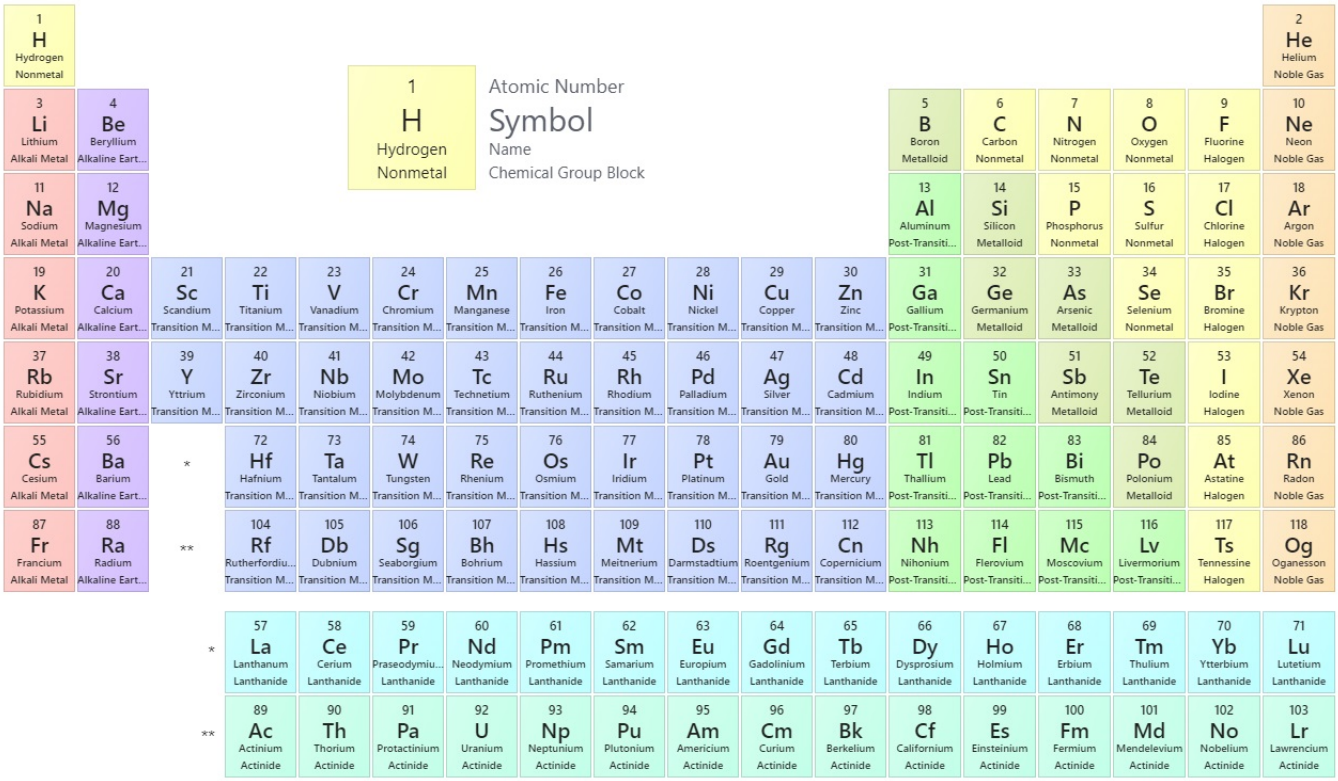


Figure **4.9.1**: A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number. An interactive Periodic table can be found Periodic Table of Elements. (Public Domain; PubChem via NIH)

Features of the Periodic Table

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

> *The word halogen comes from the Greek for "salt maker" because these elements combine with other elements to form a group of compounds called salts.*

To Your Health: Radon

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

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

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

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

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a metalloid (or semi metal), as shown in Figure **4.9.2**. A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure **4.9.2**, metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **metalloids** (or **semi-metals**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

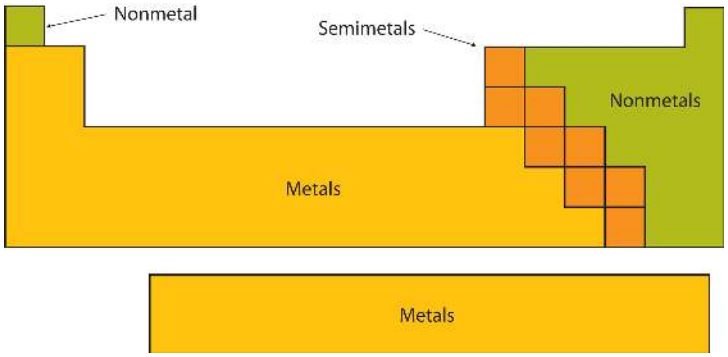


Figure **4.9.2**: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

Example 4.9.1

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

a. Se
b. Mg
c. Ge

Solution

a. In Figure **4.9.1**, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

Exercise 4.9.1

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

Answer

Indium is a metal.

Another way to categorize the elements of the periodic table is shown in Figure **4.9.3**. The first two columns on the left and the last six columns on the right are called the main group elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

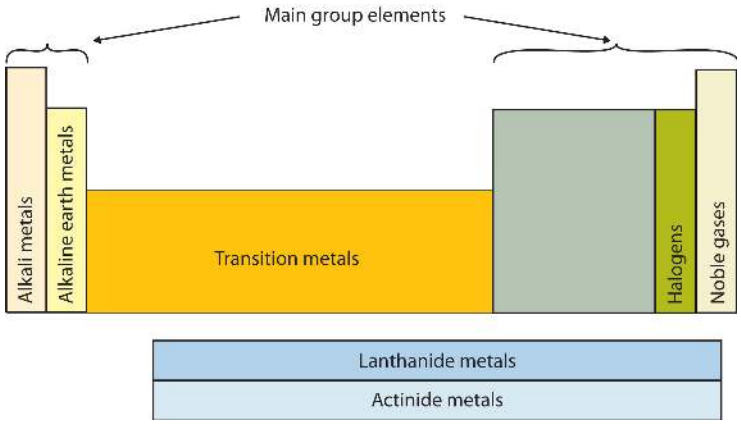


Figure **4.9.3**: Special Names for Sections of the Periodic Table. (CC BY-NC-SA; Anonymous by request)

Sections of period table: Alkali metals, alkaline earth metals, transition metals, halogens, noble gases, lanthanide metals, actinide metals.

Descriptive Names

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

Group 1: The Alkali Metals

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

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



Video: Alkali metals in water - Chemical elements: properties and reactions. (The Open University via https://youtu.be/6ZY6d6jrq-0)

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

Example 4.9.2: Groups

Provide the family or group name of each element.

a. Li
b. Ar
c. Cl

Solution

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

Exercise 4.9.2: Groups

Provide the family or group name of each element.

a. F
b. Ca
c. Kr

Answer a:

Fluorine is a halogen (Group 17).

Answer b:

Calcium is a alkaline earth metal (Group 2).

Answer c:

Krypton is a noble gas (Group 18).

Example 4.9.3: Classification of Elements

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

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

Solution

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

Exercise 4.9.3: Classification of Elements

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

a. F
b. U
c. Cu

Answer a:

Fluorine is a nonmetal.

Answer b:

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

Answer c:

Copper is a metal (and a transition metal too).

Summary

The periodic table is an arrangement of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called groups (numbered 1–18 from left to right); the seven horizontal rows are called periods. Some of the groups have widely-used common names, including the alkali metals (Group 1) and the alkaline earth metals (Group 2) on the far left, and the halogens (Group 17) and the noble gases (Group 18) on the far right.

The elements can be broadly divided into metals, nonmetals, and semi metals. Semi metals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semi metals. Metals are lustrous, good conductors of electricity, and readily shaped (they are ductile and malleable). Solid nonmetals are generally brittle and poor electrical conductors. Other important groupings of elements in the periodic table are the main group elements, the transition metals, and the inner transition metals (the lanthanides, and the actinides).

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3. Petrucci, Ralph H., Carey Bissonnette, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. Custom Edition for CHEM 2. Pearson Learning Solutions, 2010.

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4.10: The Quantum-Mechanical Model- Atoms with Orbitals

Learning Objectives

- Define quantum mechanics
- Differentiate between an orbit and an orbital.

How do you study something that seemingly makes no sense? We talk about electrons being in orbits and it sounds like we can tell where that electron is at any moment. We can draw pictures of electrons in orbit, but the reality is that we don't know exactly where they are. We are going to take a look at an area of science that even leaves scientists puzzled. When asked about quantum mechanics, Niels Bohr (who proposed the Bohr model of the atom) said: "Anyone who is not shocked by quantum theory has not understood it". Richard Feynman (one of the founders of modern quantum theory) stated: "I think I can safely say that nobody understands quantum theory." So, let's take a short trip into a land that challenges our everyday world.

Quantum Mechanics

The study of motion of large objects such as baseballs is called mechanics, or more specifically, classical mechanics. Because of the quantum nature of the electron and other tiny particles moving at high speeds, classical mechanics is inadequate to accurately describe their motion. **Quantum mechanics** is the study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality. In classical mechanics, the size and mass of the objects involved effectively obscures any quantum effects, so that such objects appear to gain or lose energies in any amounts. Particles whose motion is described by quantum mechanics gain or lose energy in small pieces called **quanta**.

One of the fundamental (and hardest to understand) principles of quantum mechanics is that the electron is both a particle and a wave. In the everyday macroscopic world of things we can see, something cannot be both. But this duality can exist in the quantum world of the submicroscopic on the atomic scale.

At the heart of quantum mechanics is the idea that we cannot accurately specify the location of an electron. All we can say is that there is a probability that it exists within this certain volume of space. The scientist Erwin Schrödinger developed an equation that deals with these calculations, which we will not pursue at this time.



Erwin Schrödinger.

Recall that in the Bohr model, the exact path of the electron was restricted to very well-defined circular **orbits** around the nucleus. An **orbital** is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

Summary

Quantum mechanics involves the study of material at the atomic level. This field deals with probabilities, since we cannot definitely locate a particle. Orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

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4.11: Quantum-Mechanical Orbitals and Electron Configurations

Learning Objectives

- Represent the organization of electrons by an electron configuration and orbital diagram.

The flight path of a commercial airliner is carefully regulated by the Federal Aviation Administration. Each airplane must maintain a distance of five miles from another plane flying at the same altitude and 2,000 feet above and below another aircraft (1,000 feet if the altitude is less than 29,000 feet). So, each aircraft only has certain positions it is allowed to maintain while it flies. As we explore quantum mechanics, we see that electrons have similar restrictions on their locations.

Orbitals

We can apply our knowledge of quantum numbers to describe the arrangement of electrons for a given atom. We do this with something called **electron configurations**. They are effectively a map of the electrons for a given atom. We look at the four quantum numbers for a given electron and then assign that electron to a specific orbital below.

s Orbitals

For any value of n, a value of $l = 0$ places that electron in an s **orbital**. This orbital is spherical in shape:

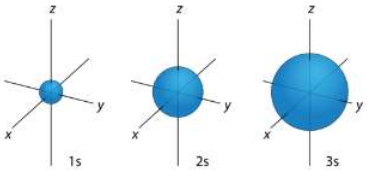


Figure 4.11.1: s orbitals have no orientational preference and resemble spheres.

p Orbitals

For the table below, we see that we can have three possible orbitals when $l = 1$. These are designated as p **orbitals** and have dumbbell shapes. Each of the p orbitals has a different orientation in three-dimensional space.

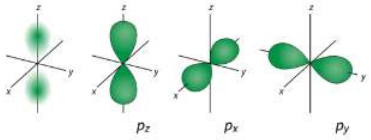


Figure 4.11.2: p orbitals have an orientational preference and resemble dumbbells.

d Orbitals

When $l = 2$, m_l values can be $-2, -1, 0, +1, +2$ for a total of five d **orbitals**. Note that all five of the orbitals have specific three-dimensional orientations.

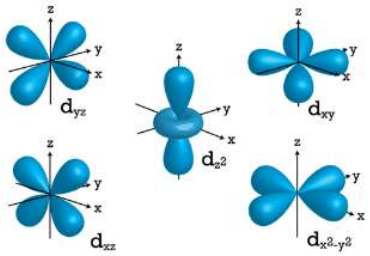


Figure 4.11.3: d orbitals have an orientational preference and exhibit complex structures.

f Orbitals

The most complex set of orbitals are the f **orbitals**. When $l = 3$, m_l values can be $-3, -2, -1, 0, +1, +2, +3$ for a total of seven different orbital shapes. Again, note the specific orientations of the different f orbitals.

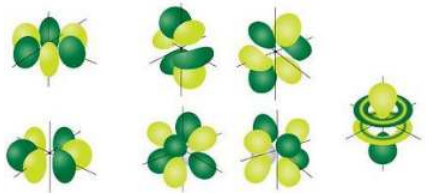


Figure 4.11.4: f orbitals have an orientational preference and exhibit quite complex structures.

Orbitals that have the same value of the principal quantum number form a **shell**. Orbitals within a shell are divided into **subshells** that have the same value of the angular quantum number. Some of the allowed combinations of quantum numbers are compared in Table 4.11.1.

Table 4.11.1: Electron Arrangement Within Energy Levels

Principal Quantum Number (n)	Allowable Sublevels	Number of Orbitals per Sublevel	Number of Orbitals per Principal Energy Level	Number of Electrons per Sublevel	Number of Electrons per Principal Energy Level
1	s	1	1	2	2
2	s	1	4	2	8
	p	3		6	
3	s	1	9	2	18
	p	3		6	
	d	5		10	
4	s	1	16	2	32
	p	3		6	
	d	5		10	
	f	7		14	

Electron Configurations

Can you name one thing that easily distinguishes you from the rest of the world? And we're not talking about DNA—that's a little expensive to sequence. For many people, it is their email address. Your email address allows people all over the world to contact you. It does not belong to anyone else, but serves to identify you. Electrons also have a unique set of identifiers in the quantum numbers that describe their location and spin. Chemists use an **electronic 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. Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies.

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

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

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

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

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

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

Be 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.

Second Period Elements

Periods refer to the horizontal rows of the periodic table. Looking at a periodic table you will see that the first period contains only the elements hydrogen and helium. This is because the first principal energy level consists of only the s sublevel and so only two electrons are required in order to fill the entire principal energy level. Each time a new principal energy level begins, as with the third element lithium, a new period is started on the periodic table. As one moves across the second period, electrons are successively added. With beryllium ($Z = 4$), the $2s$ sublevel is complete and the $2p$ sublevel begins with boron ($Z = 5$). Since there are three $2p$ orbitals and each orbital holds two electrons, the $2p$ sublevel is filled after six elements. Table 4.11.1 shows the electron configurations of the elements in the second period.

Table 4.11.2: Electron Configurations of Second-Period Elements

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

Aufbau Principle

Construction of a building begins at the bottom. The foundation is laid and the building goes up step by step. You obviously cannot start with the roof since there is no place to hang it. The building goes from the lowest level to the highest level in a systematic way. In order to create ground state electron configurations for any element, it is necessary to know the way in which the atomic sublevels are organized in order of increasing energy. Figure 4.11.5 shows the order of increasing energy of the sublevels.

The lowest energy sublevel is always the $1s$ sublevel, which consists of one orbital. The single electron of the hydrogen atom will occupy the $1s$ orbital when the atom is in its ground state. As we proceed with atoms with multiple electrons, those electrons are added to the next lowest sublevel: $2s$, $2p$, $3s$, and so on. The **Aufbau principle** states that an electron occupies orbitals in order from lowest energy to highest. The Aufbau (German: "building up, construction") principle is sometimes referred to as the "building up" principle. It is worth noting that in reality atoms are not built by adding protons and electrons one at a time, and that this method is merely an aid for us to understand the end result.

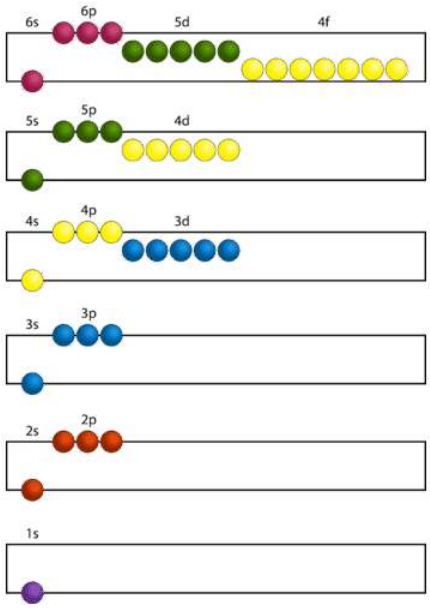


Figure **4.11.5**: Electrons are added to atomic orbitals in order from low energy (bottom of the graph) to high (top of the graph) according to the Aufbau principle. Principle energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding two electrons.

As seen in the figure above, the energies of the sublevels in different principal energy levels eventually begin to overlap. After the **3*p*** sublevel, it would seem logical that the **3*d*** sublevel should be the next lowest in energy. However, the **4*s*** sublevel is slightly lower in energy than the **3*d*** sublevel and thus fills first. Following the filling of the **3*d*** sublevel is the **4*p***, then the **5*s*** and the **4*d***. Note that the **4*f*** sublevel does not fill until just after the **6*s*** sublevel. Figure **4.11.6** is a useful and simple aid for keeping track of the order of fill of the atomic sublevels.

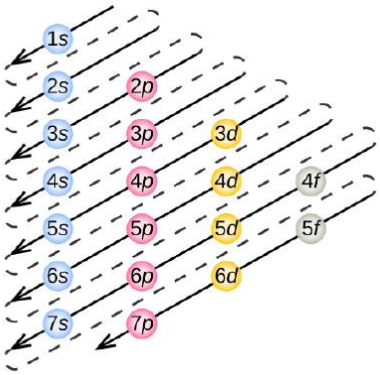


Figure **4.11.6**: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.



Video 4.11.1: Energy levels, sublevels and orbitals.

Example 4.11.1: Nitrogen Atoms

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

Solution:

Take a close look at Figure 4.11.5, and use it to figure out how many electrons go into each sublevel, and also the order in which the different sublevels get filled.

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

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

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

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

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

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

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

Example 4.11.2: Potassium Atoms

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

Solution

This time, take a close look at Figure 4.11.5.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

? Exercise 4.11.1: Magnesium and Sodium Atoms

What is the electron configuration for Mg and Na?

Answer Mg

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

Answer Na

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

Pauli Exclusion Principle

When we look at the orbital possibilities for a given atom, we see that there are different arrangements of electrons for each different type of atom. Since each electron must maintain its unique identity, we intuitively sense that the four quantum numbers for any given electron must not match up exactly with the four quantum numbers for any other electron in that atom.

For the hydrogen atom, there is no problem since there is only one electron in the **H** atom. However, when we get to helium we see that the first three quantum numbers for the two electrons are the same: same energy level, same spherical shape. What differentiates the two helium electrons is their spin. One of the electrons has a $+\frac{1}{2}$ spin while the other electron has a $-\frac{1}{2}$ spin. So the two electrons in the **1*s*** orbital are each unique and distinct from one another because their spins are different. This observation leads to the **Pauli exclusion principle**, which states that no two electrons in an atom can have the same set of four quantum numbers. The energy of the electron is specified by the principal, angular momentum, and magnetic quantum numbers. If those three numbers are identical for two electrons, the spin numbers must be different in order for the two electrons to be differentiated from one another. The two values of the spin quantum number allow each orbital to hold two electrons. Figure **4.11.7** shows how the electrons are indicated in a diagram.

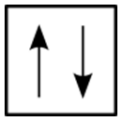


Figure **4.11.7**: In an orbital filling diagram, a square represents an orbital, while arrows represent electrons. An arrow pointing upward represents one spin direction, while an arrow pointing downward represents the other spin direction.

Hund's Rule

The last of the three rules for constructing electron arrangements requires electrons to be placed one at a time in a set of orbitals within the same sublevel. This minimizes the natural repulsive forces that one electron has for another. **Hund's rule** states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron and that each of the single electrons must have the same spin. The figure below shows how a set of three ***p*** orbitals is filled with one, two, three, and four electrons.

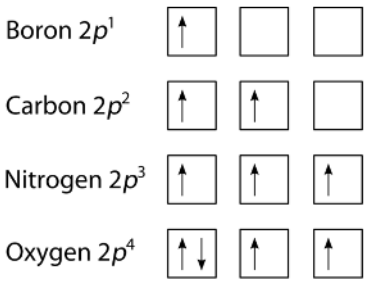


Figure 4.11.8: The $2p$ sublevel, for the elements boron ($Z = 5$), carbon ($Z = 6$), nitrogen ($Z = 7$), and oxygen ($Z = 8$). According to Hund's rule, as electrons are added to a set of orbitals of equal energy, one electron enters each orbital before any orbital receives a second electron.

Orbital Filling Diagrams

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

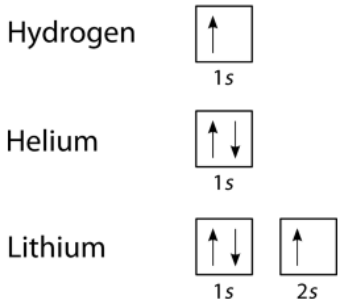


Figure 4.11.9: Orbital filling diagrams for hydrogen, helium, and lithium.

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

The filling diagram for carbon is shown in Figure 4.11.10. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital.

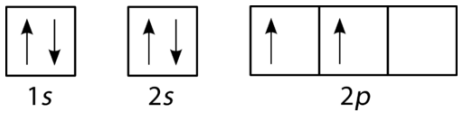


Figure 4.11.10: Orbital filling diagram for carbon.

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

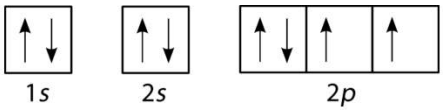


Figure 4.11.11: Orbital filling diagram for oxygen.

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

Example 4.11.3: Carbon Atoms

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

Solution

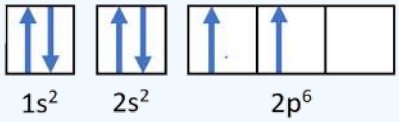
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

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

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

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

Step 3: Think about your result.

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

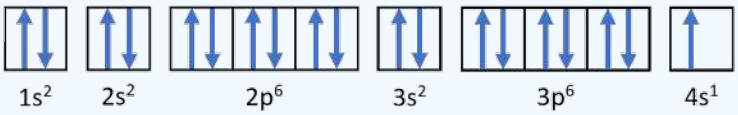
Exercise 4.11.2: Electronic Configurations

Write the electron configurations and orbital diagrams for

a. Potassium atom: **K**
b. Arsenic atom: **As**
c. Phosphorus atom: **P**

Answer a:

Potassium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$



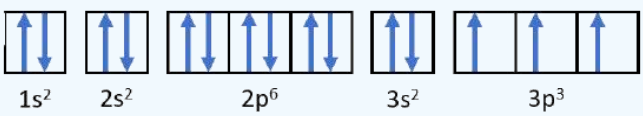
Answer b:

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



Answer c:

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



The Atom Neighborhood



Figure **4.11.12**: The atom neighborhood. Source: Dr. Binh Dao, Sacramento City College.

Summary

There are four different classes of electron orbitals. These orbitals are determined by the value of the angular momentum quantum number ℓ. An orbital is a wave function for an electron defined by the three quantum numbers, n, ℓ and m_ℓ. Orbitals define regions in space where you are likely to find electrons. *s* orbitals ($\ell = 0$) are spherical shaped. *p* orbitals ($\ell = 1$) are dumb-bell shaped. The three possible *p* orbitals are always perpendicular to each other.

Electron configuration notation simplifies the indication of where electrons are located in a specific atom. Superscripts are used to indicate the number of electrons in a given sublevel. The Aufbau principle gives the order of electron filling in an atom. It can be used to describe the locations and energy levels of every electron in a given atom. Hund's rule specifies the order of electron filling within a set of orbitals. Orbital filling diagrams are a way of indicating electron locations in orbitals. The Pauli exclusion principle specifies limits on how identical quantum numbers can be for two electrons in the same atom.

Vocabulary

principal quantum number (*n*)
: Defines the energy level of the wave function for an electron, the size of the electron's standing wave, and the number of nodes in that wave.

quantum numbers
: Integer numbers assigned to certain quantities in the electron wave function. Because electron standing waves must be continuous and must not "double over" on themselves, quantum numbers are restricted to integer values.

Contributions & Attributions

-
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4.12: Electron Configurations and the Periodic Table

Learning Objectives

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

Previously, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure **4.12.1**. 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.

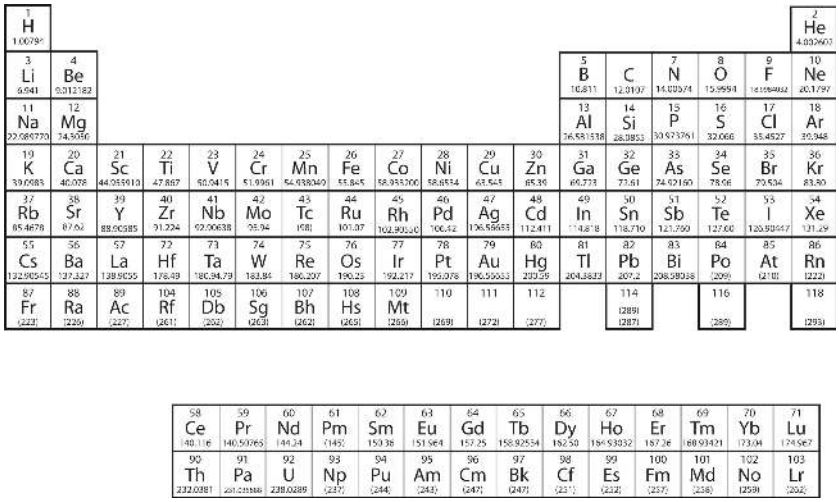


Figure **4.12.1**: The Periodic Table

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 **4.12.2**)

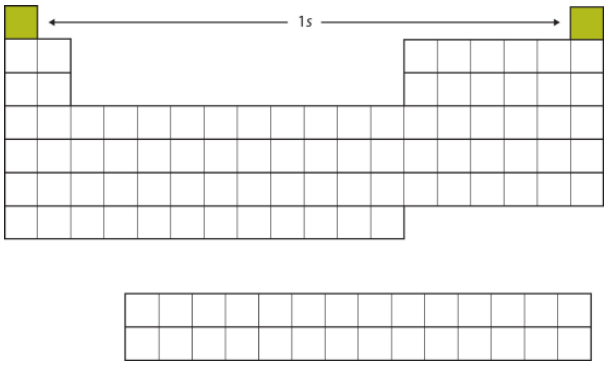


Figure **4.12.2**: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure **4.12.3** shows that these two elements are adjacent on the periodic table.

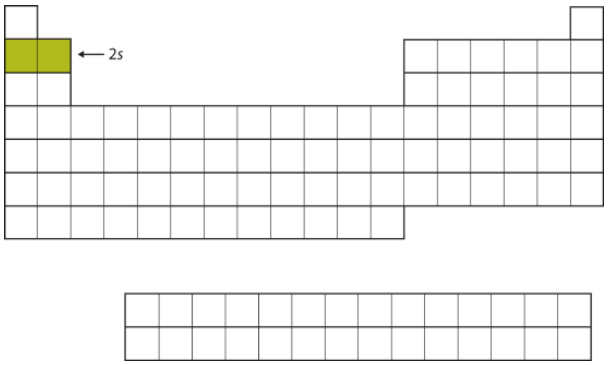


Figure 4.12.3: The 2*s* Subshell. In Li and Be, the 2*s* subshell is being filled.

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 4.12.4).

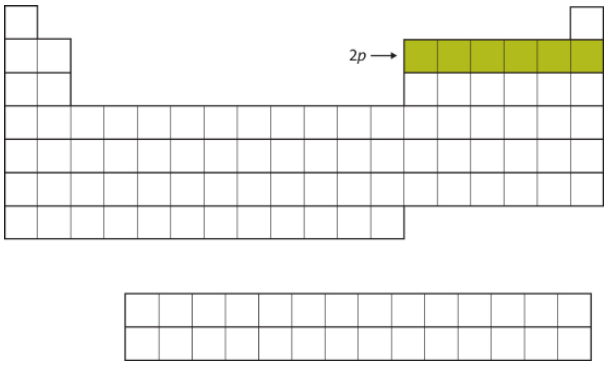


Figure 4.12.4: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 4.12.5).

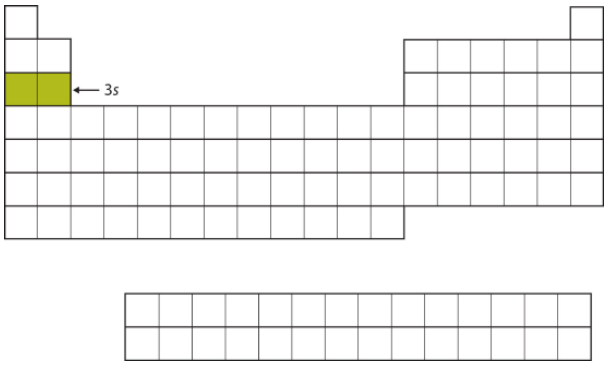


Figure 4.12.5: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 4.12.6).

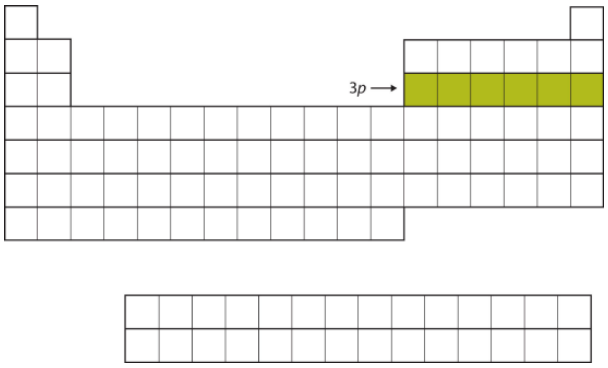


Figure 4.12.6: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 4.12.7).

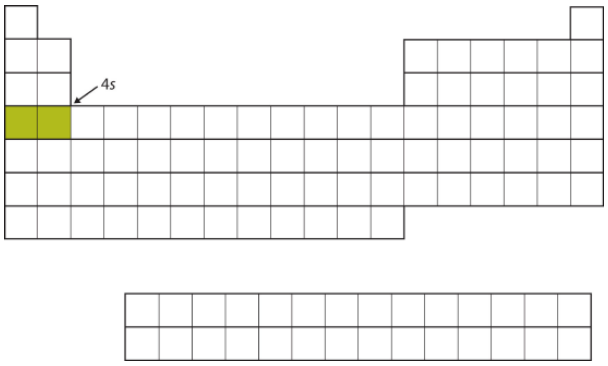


Figure 4.12.7: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

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 4.12.8).

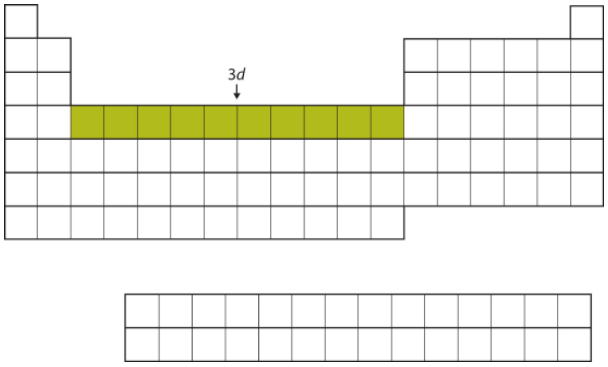


Figure 4.12.8: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 4.12.9 shows the blocks of the periodic table.

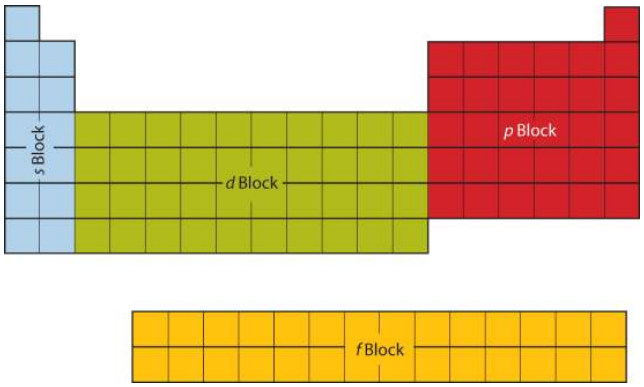


Figure **4.12.9**: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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:

Electrons, electron configurations, and the valence shell electron configuration highlighted.

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

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 **4.12.10**. 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 $[Ar]4s^23d^{10}4p^4$, as expected.

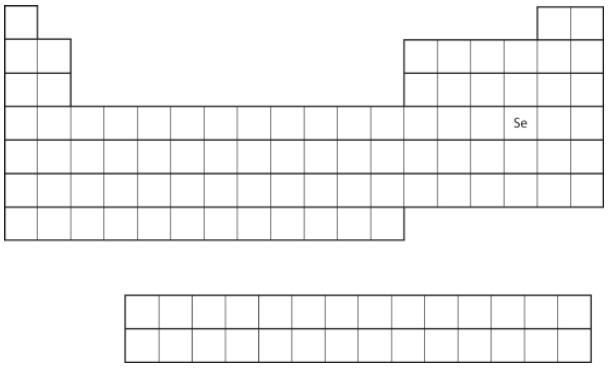


Figure **4.12.10**: Selenium on the Periodic Table

Example 4.12.1: Predicting Electron Configurations

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure **4.12.11**).

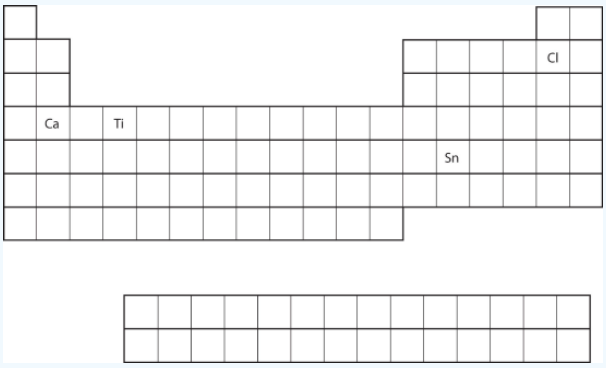


Figure **4.12.11**: Various Elements on the Periodic Table

a. Ca
b. Sn

Solution

a. Ca is located in the second column of the *s* block. We expect that its electron configuration should end with s^2. Calcium's electron configuration is $[Ar]4s^2$.
b. 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 4.12.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure **4.12.11**.

a. Ti
b. Cl

Answer a

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

Answer b

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

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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4.13: Ions - Losing and Gaining Electrons

Learning Objectives

- Define the two types of ions.

Atoms tend to lose, gain, or share some valance electrons, making bonds to acquire the electron configuration of the nearest noble gas, i.e., usually eight valence electrons for the main group elements, called an octet. Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while others lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called **cations**. Most metals become cations when they make ionic compounds.

Cations

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

$$Na \rightarrow Na^+ + e^-$$

The cation produced in this way, Na^+, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure 4.13.1 is a graphical depiction of this process.

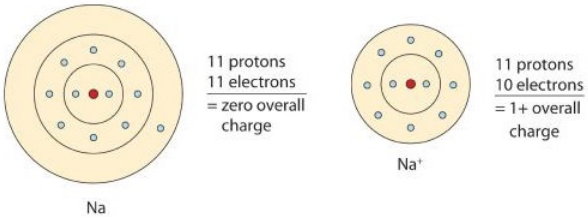


Figure 4.13.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge. Neutral sodium atom on left has 11 protons and 11 electrons. Sodium ion on right has 11 protons and 10 electrons, with a +1 overall charge.

Anions

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

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

$$e^- + Cl \longrightarrow Cl^-$$

In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. Figure 4.13.2 is a graphical depiction of this process.

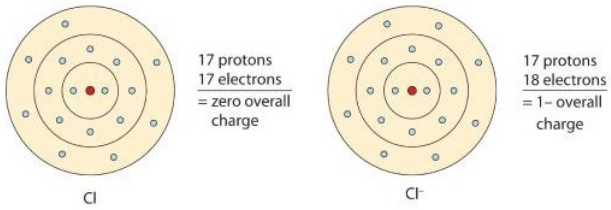


Figure **4.13.2**: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge. Neutral chlorine atom on left has 17 protons and 17 electrons. Sodium ion on right has 17 protons and 18 electrons, with a -1 overall charge.

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

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure **4.13.3** shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a ion with multiple charges. The barium cation is written Ba^{2+}, not Ba^{+2}.

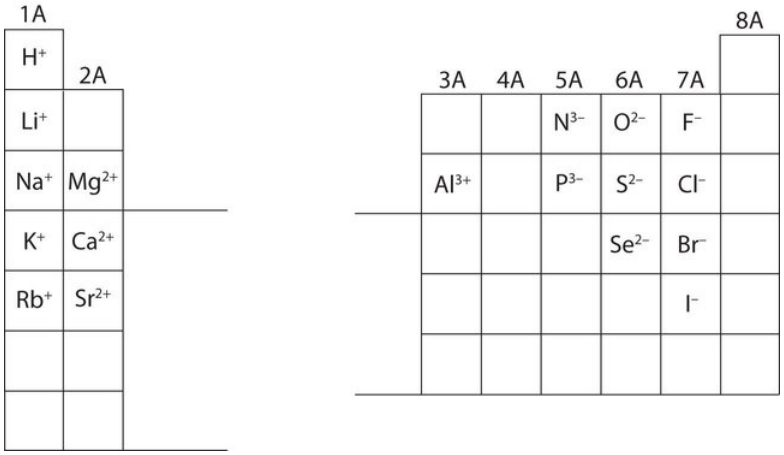


Figure **4.13.3**: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

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4.14: Isotopes - When the Number of Neutrons Varies

Learning Objectives

- Explain what isotopes are and how an isotope affects an element's atomic mass.
- Determine the number of protons, electrons, and neutrons of an element with a given mass number.

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

An Example: Hydrogen Isotopes

Hydrogen is an example of an element that has isotopes. Three isotopes of hydrogen are modeled in Figure **4.14.1**. Most hydrogen atoms have just one proton, one electron, and lack a neutron. These atoms are just called hydrogen. Some hydrogen atoms have one neutron as well. These atoms are the isotope named deuterium. Other hydrogen atoms have two neutrons. These atoms are the isotope named tritium.

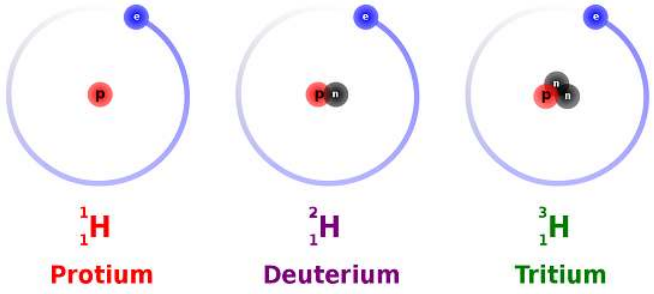


Figure **4.14.1**: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

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

Example 4.14.1: Lithium Isotopes

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

Solution

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

a.

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

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

b.

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

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

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

Stability of Isotopes

Atoms need a certain ratio of neutrons to protons to have a stable nucleus. Having too many or too few neutrons relative to protons results in an unstable, or radioactive, nucleus that will sooner or later break down to a more stable form. This process is called radioactive decay. Many isotopes have radioactive nuclei, and these isotopes are referred to as radioisotopes. When they decay, they release particles that may be harmful. This is why radioactive isotopes are dangerous and why working with them requires special suits for protection. The isotope of carbon known as carbon-14 is an example of a radioisotope. In contrast, the carbon isotopes called carbon-12 and carbon-13 are stable.

This whole discussion of isotopes brings us back to Dalton's Atomic Theory. According to Dalton, atoms of a given element are identical. But if atoms of a given element can have different numbers of neutrons, then they can have different masses as well! How did Dalton miss this? It turns out that elements found in nature exist as constant uniform mixtures of their naturally occurring isotopes. In other words, a piece of lithium always contains both types of naturally occurring lithium (the type with 3 neutrons and the type with 4 neutrons). Moreover, it always contains the two in the same relative amounts (or "relative abundance"). In a chunk of lithium, **93%** will always be lithium with 4 neutrons, while the remaining **7%** will always be lithium with 3 neutrons.

Dalton always experimented with large chunks of an element—chunks that contained all of the naturally occurring isotopes of that element. As a result, when he performed his measurements, he was actually observing the averaged properties of all the different isotopes in the sample. For most of our purposes in chemistry, we will do the same thing and deal with the average mass of the atoms. Luckily, aside from having different masses, most other properties of different isotopes are similar.

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

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



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

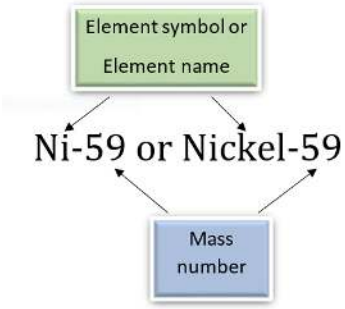
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

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

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

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

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



Example 4.14.2: Potassium-40

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

Solution

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

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

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

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

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

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

Example 4.14.3: Zinc-65

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

Solution

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

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

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

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

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

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

Exercise 4.14.3

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

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

Answer a:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 neutrons

Answer c:

20 protons, 20 electrons, 25 neutrons

Answer d:

38 protons, 38 electrons, 52 neutrons

Summary

- The number of protons is always the same in atoms of the same element.
- The number of neutrons can be different, even in atoms of the same element.
- Atoms of the same element that contain the same number of protons, but different numbers of neutrons, are known as **isotopes**.
- Isotopes of any given element all contain the same number of protons, so they have the same atomic number (for example, the atomic number of helium is always 2).
- Isotopes of a given element contain different numbers of neutrons, therefore, different isotopes have different mass numbers.

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4.15: Atomic Mass - The Average Mass of an Element's Atoms

Learning Objectives

- Explain what is meant by the atomic mass of an element.
- Calculate the atomic mass of an element from the masses and relative percentages of the isotopes of the element.

In chemistry we very rarely deal with only one isotope of an element. We use a mixture of the isotopes of an element in chemical reactions and other aspects of chemistry, because all of the isotopes of an element react in the same manner. That means that we rarely need to worry about the mass of a specific isotope, but instead we need to know the average mass of the atoms of an element. Using the masses of the different isotopes and how abundant each isotope is, we can find the average mass of the atoms of an element. The **atomic mass** of an element is the weighted average mass of the atoms in a naturally occurring sample of the element. Atomic mass is typically reported in atomic mass units.

Calculating Atomic Mass

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

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

Look carefully to see how this equation is used in the following examples.

Example 4.15.1: Boron Isotopes

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

Solution

Boron has two isotopes. We will use the equation:

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

- Isotope 1: $\%_1 = 0.20$ (Write all percentages as decimals), $\text{mass}_1 = 10$
- Isotope 2: $\%_2 = 0.80$, $\text{mass}_2 = 11$

Substitute these into the equation, and we get:

$$\text{Atomic mass} = (0.20)\,(10) + (0.80)\,(11)$$

$$\text{Atomic mass} = 10.8\ \text{amu}$$

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

Example 4.15.2: Neon Isotopes

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

Solution

Neon has three isotopes. We will use the equation:

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

- Isotope 1: $\%_1 = 0.9092$ (write all percentages as decimals), $\text{mass}_1 = 19.99$

- Isotope 2: $\%_2 = 0.003$, $\text{mass}_2 = 20.99$
- Isotope 3: $\%_3 = 0.0885$, $\text{mass}_3 = 21.99$

Substitute these into the equation, and we get:

$$\text{Atomic mass} = (0.9092)(19.99) + (0.003)(20.99) + (0.0885)(21.99)$$

$$\text{Atomic mass} = 20.17\ \text{amu}$$

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

The periodic table gives the atomic mass of each element. The atomic mass is a number that usually appears below the element's symbol in each square. Notice that the atomic mass of boron (symbol B) is 10.8, which is what we calculated in Example 4.15.1, and the atomic mass of neon (symbol Ne) is 20.8, which is what we calculated in Example 4.15.2. Take time to notice that not all periodic tables have the atomic number above the element's symbol and the mass number below it. If you are ever confused, remember that the atomic number should always be the smaller of the two and will be a whole number, while the atomic mass should always be the larger of the two and will be a decimal number.

? Exercise 4.15.1

Chlorine has two naturally occurring isotopes. In a sample of chlorine, 75.77% of the atoms are Cl-35, with a mass of $34.97\ \text{amu}$. Another 24.23% of the atoms are Cl-37, with a mass of $36.97\ \text{amu}$. What is the atomic mass of chlorine?

Answer

35.45 amu

Summary

- An element's atomic mass is the weighted average of the masses of the isotopes of an element
- An element's atomic mass can be calculated provided the relative abundance of the element's naturally occurring isotopes and the masses of those isotopes are known.
- The periodic table is a convenient way to summarize information about the different elements. In addition to the element's symbol, most periodic tables will also contain the element's atomic number and the element's atomic mass.

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CHAPTER OVERVIEW

5: Molecules and Compounds

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There are many substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multi-atom 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.

5.1: Sugar and Salt
5.2: Compounds Display Constant Composition
5.3: Chemical Formulas - How to Represent Compounds
5.4: A Molecular View of Elements and Compounds
5.5: Writing Formulas for Ionic Compounds
5.6: Nomenclature- Naming Compounds
5.7: Naming Ionic Compounds
5.8: Naming Molecular (Covalent) Compounds
5.9: Naming Acids
5.10: Nomenclature Summary

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5.1: Sugar and Salt

Sodium chloride, also known as table salt, is an ionic compound with the chemical formula NaCl, representing a 1:1 ratio of sodium and chloride ions. It is commonly used as a condiment and food preservative. Salt can be created by adding two very reactive elements together: sodium ($\mathrm{Na(s)}$ metal and chlorine ($\mathrm{Cl_2(g)}$ gas.

$$\mathrm{2\,Na(s) + Cl_2(g) \rightarrow 2\,NaCl(s)} \tag{5.1.1}$$

The element sodium (Figure 5.1.1*a*) is a very reactive metal; given the opportunity, it will react with the sweat on your hands and form sodium hydroxide, which is a very corrosive substance. The element chlorine (Figure 5.1.1*b*) is a pale yellow, corrosive gas that should not be inhaled due to its poisonous nature. Bring these two hazardous substances together, however, and they react to make the ionic compound sodium chloride (Figure 5.1.1*c*), known simply as salt.

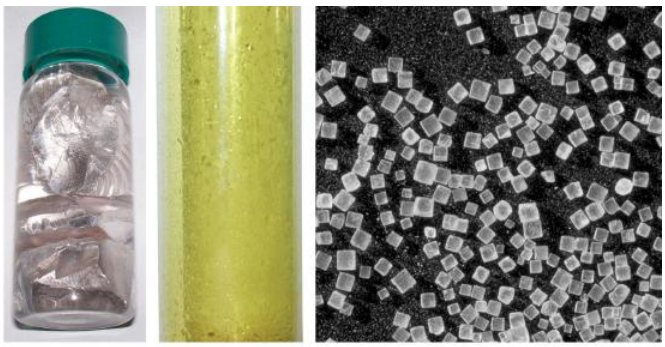


Figure 5.1.1: Sodium + Chlorine = Sodium Chloride (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride—salt—which is necessary for our survival. Source: Photo on the left courtesy of reenhorn1 and photo in the center courtesy of Benjah-bmm27. Photo on the right © Thinkstock.

Salt is necessary for life. $\mathrm{Na^+}$ ions are one of the main ions in the human body and are necessary to regulate the fluid balance in the body. $\mathrm{Cl^-}$ ions are necessary for proper nerve function and respiration. Both of these ions are supplied by salt. The taste of salt is one of the fundamental tastes; salt is probably the most ancient flavoring known, and one of the few rocks we eat. Clearly when the elemental sodium and chlorine combine (Equation 5.1.1), the resulting salt product has radically different properties (both physical and chemical). This reaction is spectacular to observe (Video 5.1.1).



Video* 5.1.1*: *Making Table Salt using Sodium Metal and Chlorine gas*

Another compound is sugar, which is the generic name for sweet, soluble carbohydrates, many of which are used in food. Sugar has the chemical formulate $\mathrm{C_{12}H_{22}O_{11}}$ and is constructed from different elements than salt: carbon, hydrogen and oxygen. While sugar qualitatively resembles table salt (often confused in the kitchen), the two have distinctly different physical and chemical properties. There are various types of sugar derived from different sources. While sugar is made with carbon, hydrogen, and oxygen, it is considerably harder to synthesize from its constituent elements than table salt is (Equation 5.1.1). However, the thermal

decomposition is considerably easier and can be represented as a dehydration of sucrose to pure carbon and water vapor in Equation 5.1.2, and demonstrated in Video 5.1.2.

$$\mathrm{C_{12}H_{22}O_{11}\,(s) + heat \longrightarrow 12\,C\,(s) + 11\,H_2O\,(g)} \tag{5.1.2}$$



Video* 5.1.2*: *A science experiment in the kitchen shows what happens to sugar molecules when they are heated. The experiment did not disappoint!*

As with salt, sugar has radically different properties (both physical and chemical) than its constituent elements. This difference in properties, of constituent elements and compounds, is a central feature of chemical reactions.

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5.2: Compounds Display Constant Composition

When building a house, the starting point is a blueprint of what the house will look like. The plan states how many windows and what kind, how many doors and what style, how many rooms and what type (bedroom, kitchen, other). The blueprint shows how the different pieces will go together to make the house. As long as the blueprint is followed and exactly the same items are used, the house will be identical to its blueprint.

Compounds

A **compound** is a substance that contains two or more elements chemically combined in a fixed proportion. The elements carbon and hydrogen combine to form many different compounds. One of the simplest is called methane, in which there are always four times as many hydrogen particles as carbon particles. Methane is a pure substance because it always has the same composition. However, it is not an element because it can be broken down into simpler substances—carbon and hydrogen.

Recall that the components of a mixture can be separated from one another by physical means. This is not true for a compound. Table salt is a compound consisting of equal parts of the elements sodium and chlorine. Salt cannot be separated into its two elements by filtering, distillation, or any other physical process. Salt and other compounds can only be decomposed into their elements by a chemical process. A **chemical change** is a change that produces matter with a different composition. Many compounds can be decomposed into their elements by heating. When sugar is heated, it decomposes into carbon and water. Water is still a compound, but one which cannot be broken down into hydrogen and oxygen by heating. Instead, the passage of an electrical current through water will produce hydrogen and oxygen gases.

The properties of compounds are generally very different than the properties of the elements from which the compound is formed. Sodium is an extremely reactive soft metal that cannot be exposed to air or water. Chlorine is a deadly gas. The compound sodium chloride is a white solid which is essential for all living things (see below).

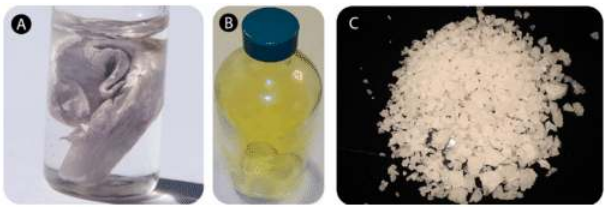


Figure **5.2.1**: (A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine.

Summary

- A compound is a substance that contains two or more elements chemically combined in a fixed proportion.
- A chemical change is a change that produces matter with a different composition.

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5.3: 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 $\mathbf{H_2O}$. 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 $\mathbf{H_2SO_4}$.

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 $\mathbf{Ca_3(PO_4)_2}$ 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:

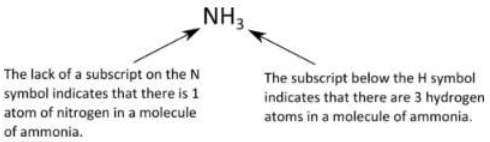


Figure 5.3.1: The molecular formula for ammonia. NH3. There is one atom of nitrogen and 3 atoms of hydrogen in a molecule of ammonia.

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 $\mathbf{N_3H}$ 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 $\mathbf{C_6H_{12}O_6}$. Since each of the subscripts is divisible by 6, the empirical formula for glucose is $\mathbf{CH_2O}$. When chemists analyze an unknown compound, often the first step is to determine its empirical formula.

- molecular formula: $\mathbf{C_6H_{12}O_6}$
- empirical formula: $\mathbf{CH_2O}$

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 $\mathbf{H_2O}$ or $\mathbf{P_2O_5}$, 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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5.4: A Molecular View of Elements and Compounds

Learning Objectives

- Classify substances as atomic elements, molecular elements, molecular compounds, or ionic compounds.

Atomic Elements

Most elements exist with **individual atoms** as their basic unit. 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.

Molecular Elements

There are many substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multi-atom 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 5.4.1: Elements That Exist as Diatomic Molecules

Hydrogen, H	Oxygen	Nitrogen	Fluorine	Chlorine	Bromine	Iodine

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules—a molecule with only two atoms (Table 5.4.1). 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 5.4.1).

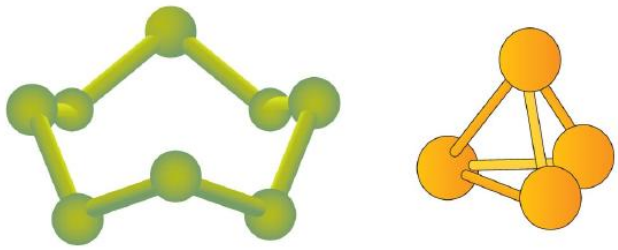


Figure 5.4.1: Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure 5.4.1 shows two examples of how molecules will be represented 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.

Ionic Compounds

The elements in the periodic table are divided into specific groupings; the metals, the non-metals, the semi-metals, and so on. These groupings are largely based on physical properties and on the tendency of the various elements to bond with other elements by forming either an ionic or a covalent bond. As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). The basic unit of ionic compounds is the **formula unit**.

Molecular Compounds

Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds. Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals) and silicon dioxide (SiO_2) will also be a covalently bound molecule (a semi-metal and a non-metal). The basic unit of molecular compounds is the **molecule**.

Example 5.4.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. Fe
b. PCl_3
c. LiBr
d. P_4
e. oxygen gas

Solution

a. **Fe** (iron) is an element that is represented with no subscript, so it is an **atomic element**.
b. **PCl_3** is made up of two nonmetals, so it is a **molecular compound**.
c. **LiBr** is made up of lithium, a metal, and bromine, a nonmetal, so it is an **ionic compound**.
d. **P_4** is a substance that is made up of four atoms of the same element, so it is a **molecular element**.
e. The formula for **oxygen gas** is **O_2** so it is a molecular element.

Exercise 5.4.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. I_2
b. He
c. H_2O
d. Al
e. CuCl

Answer a:
molecular element

Answer b:
atomic element

Answer c:
molecular compound

Answer d:
atomic element

Answer e:
ionic compound

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5.5: 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 5.5.1: 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 5.5.2: 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 5.5.2

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

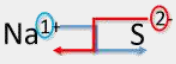
> *Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.*

Example 5.5.3: 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 5.5.3

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 5.5.1 lists the most common polyatomic ions.

Table 5.5.1: Some Polyatomic Ions

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

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.

Writing Formulas for Ionic Compounds Containing Polyatomic Ions

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

Example 5.5.4: 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 5.5.5

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 5.5.5

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 5.5.6

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 5.5.6

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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5.6: Nomenclature- Naming Compounds

Nomenclature is the process of naming chemical compounds so that they can be easily identified as separate chemicals. The primary function of chemical nomenclature is to ensure that a spoken or written chemical name leaves no ambiguity concerning which chemical compound the name refers to—each chemical name should refer to a single substance. A less important aim is to ensure that each substance has a single name, although a limited number of alternative names is acceptable in some cases. Preferably, the name also conveys some information about the structure or chemistry of a compound. A common name will often suffice to identify a chemical compound in a particular set of circumstances. To be more generally applicable, the name should indicate at least the chemical formula. To be more specific still, the three-dimensional arrangement of the atoms may need to be specified.

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5.7: Naming Ionic Compounds

Learning Objectives

- To use the rules for naming ionic compounds.

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

Naming Ions

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

We have seen that some elements lose different numbers of electrons, producing ions of different charges (Figure 3.3). Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

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

Table **5.7.1**: The Modern and Common System of Cation Names

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

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table **5.7.1** lists the elements that use the common system, along with their respective cation names.

Table **5.7.2**: Some Monatomic Anions

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

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table 5.7.2 lists the names of some common monatomic ions. The polyatomic ions have their own characteristic names, as discussed earlier.

Example 5.7.1

Name each ion.

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

Solution

a. the calcium ion
b. the sulfide ion
c. the sulfite ion
d. the ammonium ion
e. the copper(I) ion or the cuprous ion

Exercise 5.7.1

Name each ion.

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

Answer a:
iron(II) ion

Answer b:
iron(III) ion

Answer c:
sulfate ion

Answer d:

barium ion

Answer e:

hydrogen carbonate ion or bicarbonate ion

Example 5.7.2

Write the formula for each ion.

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

Solution

a. Br^-
b. PO_4^{3-}
c. Cu^{2+}
d. Mg^{2+}

Exercise 5.7.2

Write the formula for each ion.

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

Answer a:

F^-

Answer b:

CO_3^{2-}

Answer c:

Sn^{2+}

Answer d:

K^+

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

A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**. The metal cation is named first, followed by the nonmetal anion as illustrated in Figure **5.7.1** for the compound $BaCl_2$. The word *ion* is dropped from both parts.

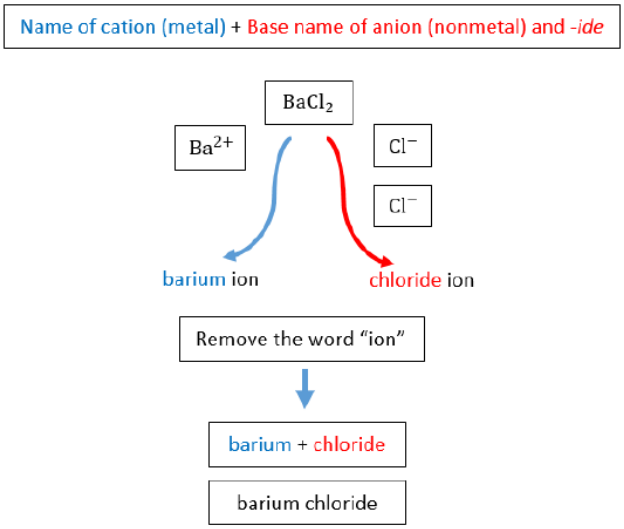


Figure **5.7.1**: Naming $BaCl_2$
Naming formula: Name of metal cation + base
name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

✔ Example 5.7.3: Naming Ionic Compounds

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. KCl

Solution

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

? Exercise 5.7.3

Name each ionic compound.

a. AgI
b. MgO
c. Ca_3P_2

Answer a:
silver iodide

Answer b:
magnesium oxide

Answer c:
calcium phosphide

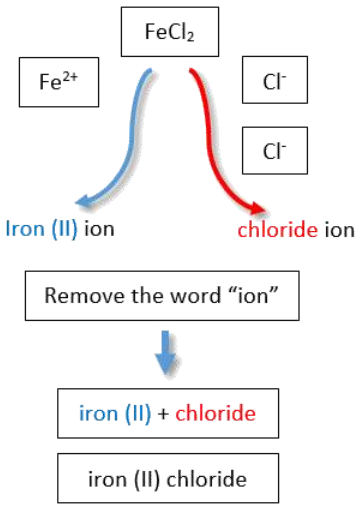
Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

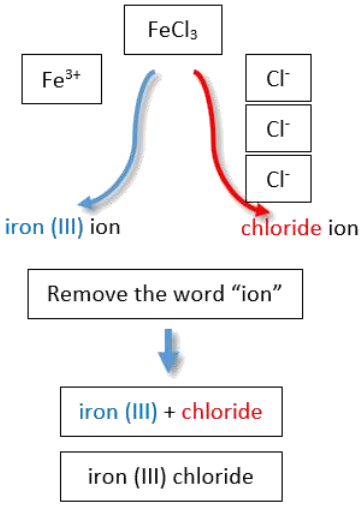
If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron

ion has a 2+ charge because there are two Cl^- ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride (Figure **5.7.2**).

Table **5.7.3**: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Modern/Stock System.

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

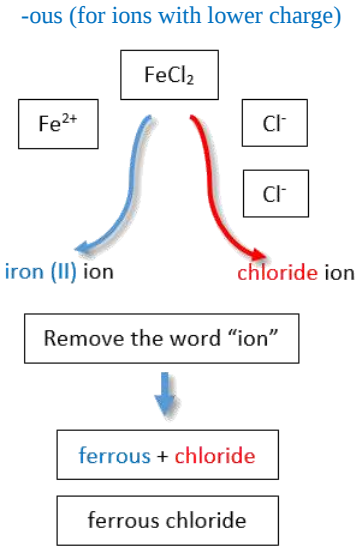


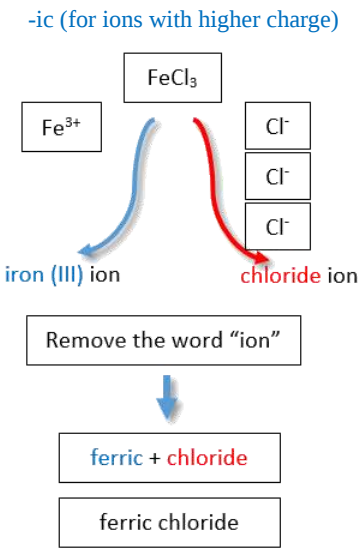


If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure **5.7.3**) .

Table **5.7.4**: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Old/Common System.

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





Example 5.7.4:

Name each ionic compound.

a. Co_2O_3
b. FeCl2

Solution

Solutions to Example 5.7.4

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

Exercise 5.7.4

Name each ionic compound.

a. $AuCl_3$
b. PbO_2
c. CuO

Answer a:

gold(III) chloride

Answer b:

lead(IV) oxide

Answer c:

copper(II) oxide

Naming Ionic Compounds with Polyatomic Ions

The process of naming ionic compounds with polyatomic ions is the same as naming binary ionic compounds. The cation is named first, followed by the anion. One example is the ammonium sulfate compound in Figure **5.7.6**.

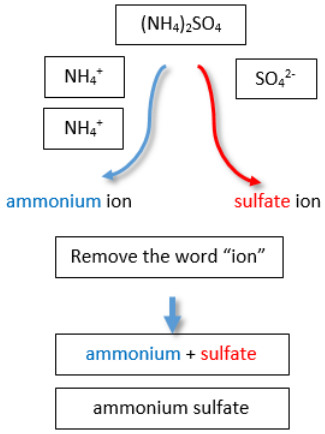


Figure **5.7.2**: Naming Ionic Compounds with Polyatomic Ions

Example 5.7.5: Naming Ionic Compounds

Write the proper name for each ionic compound.

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

Solution

Solutions to Example 5.7.5

Explanation	Answer
a. The ammonium ion has a 1+ charge and the sulfide ion has a 2− charge. Two ammonium ions need to balance the charge on a single sulfide ion. The compound’s name is ammonium sulfide.	ammonium sulfide
b. The ions have the same magnitude of charge, one of each (ion) is needed to balance the charges. The name of the compound is aluminum phosphate.	aluminum phosphate
c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, three iron(II) ions are needed, and to get 6−, two phosphate ions are needed . The compound’s name is iron(II) phosphate.	iron(II) phosphate

Exercise 5.7.5A

Write the proper name for each ionic compound.

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

Answer a:

ammonium phosphate

Answer b:

cobalt(III) nitrite

Figure 5.7.1 is a synopsis of how to name simple ionic compounds.

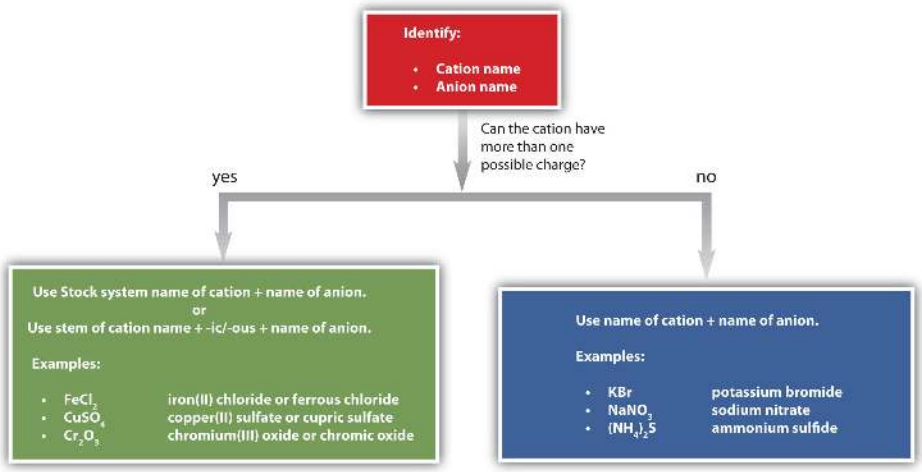


Figure 5.7.3: A Guide to Naming Simple Ionic Compounds.

? Exercise 5.7.5*B*

Name each ionic compound.

a. $ZnBr_2$
b. Al_2O_3
c. $(NH_4)_3PO_4$
d. AuF_3
e. AgF

Answer a:

zinc bromide

Answer b:

aluminum oxide

Answer c:

ammonium phosphate

Answer d:

gold(III) fluoride or auric fluoride

Answer e:

silver fluoride

Summary

- Ionic compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.
- Some anions have multiple forms and are named accordingly with the use of roman numerals in parentheses.
- Ternary compounds are composed of three or more elements.

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5.8: Naming Molecular (Covalent) 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.

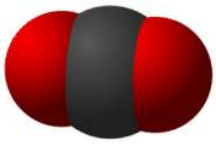


Figure 5.8.1: Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

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}.



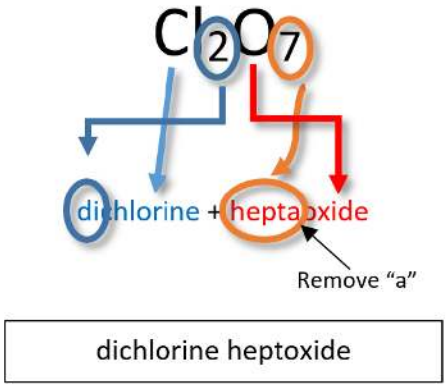
Figure 5.8.2: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

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 5.8.1 lists these numerical prefixes.

Table 5.8.1: 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 5.8.2.

Table 5.8.2

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 5.8.1

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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5.9: Naming Acids

A spot test for gold has been in use for decades. The sample is first treated with nitric acid. Other metals may react or dissolve in this acid, but gold will not. Then the sample is added to a mixture of nitric acid and hydrochloric acid. Gold will only dissolve in this mixture. The term "acid test" arose from the California gold rush in the late 1840's when this combination was used to test for the presence of real gold. It has since come to mean, "tested and approved" in a number of fields.

Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions (H^+) when dissolved in water.



Figure 5.9.1: (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

This is a different type of compound than the others we have seen so far. Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like $NaCl$. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$HCl \rightarrow H^+ + Cl^-$$

Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic.

Naming Binary acids (in aqueous form)

A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. The acid name begins with the prefix *hydro-*. followed by the base name of the anion, followed by the suffix *-ic*.

Hydro- and Base name of Non metal and *-ic + acid*

Example: $HCl_{(aq)}$

Cl^-, chloride ion

hydrochloric acid

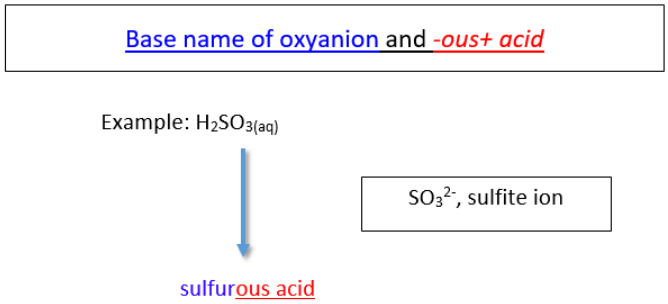
Formula for naming acids: Hydro- and Base name of nonmetal and -ic + acid. Example: HCl is hydrochloric acid.

Naming Oxyacids

An **oxyacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

a. Oxyanions with ***-ite*** ending.

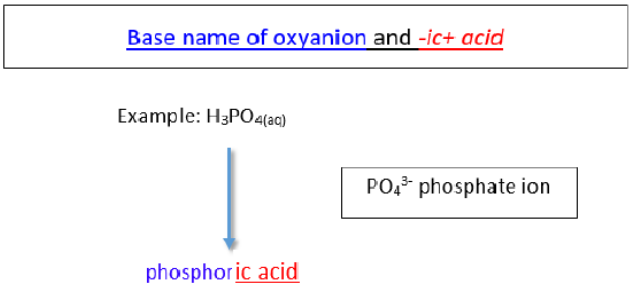
The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.



Formula for naming oxyanions with -ite ending: Base name of oxyanion and -ous + acid. Example: H2SO3 is sulfurous acid.

b. Oxyanions with ***-ate*** ending.

The name of the acid is the root of the anion followed by the suffix ***-ic***. There is no prefix.

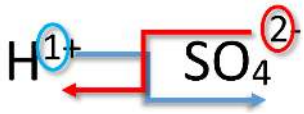


Formula for naming oxyanions with -ate ending: Base name of oxyanion and -ic + acid. Example: H3PO4 is phosphoric acid.

> **Note**
>
> The base name for sulfur containing oxyacid is ***sulfur-*** instead of just ***sulf-***. The same is true for a phosphorus containing oxyacid. The base name is ***phosphor-*** instead of simply ***phosph-***.

Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the H^+ ions. Another way to think about writing the correct formula is to utilize the crisscross method, shown below for sulfuric acid.



H2SO4: H has +1 charge and SO4 has -2 charge, so there must be 2 H+ and 1 SO4 for the charges to balance out.

Formula: H_2SO_4

Figure 5.9.2: *Crisscross approach to writing formula for sulfuric acid.*

Summary

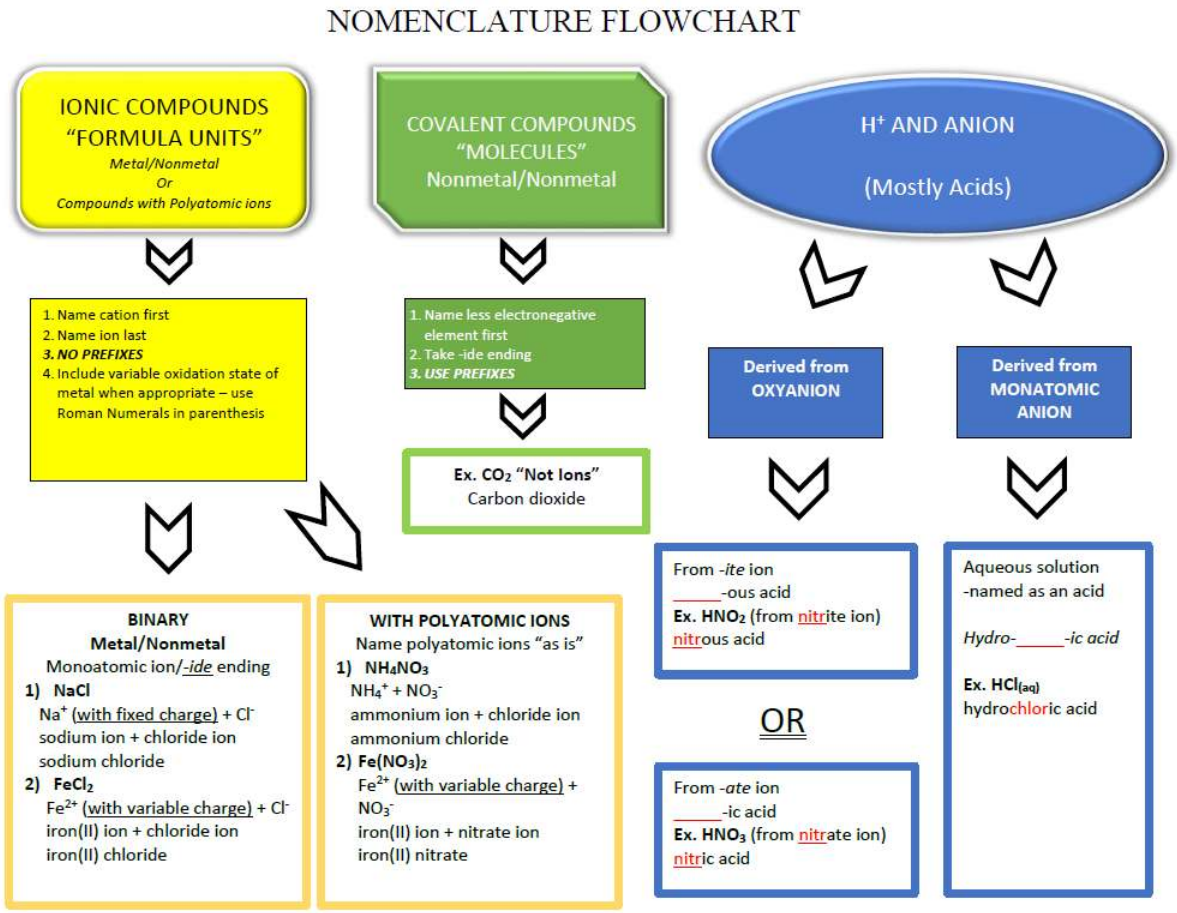
- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxyacids contain hydrogen, oxygen, and one other element.

- The name of the acid is based on the anion attached to the hydrogen.

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5.10: Nomenclature Summary



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CHAPTER OVERVIEW

6: Chemical Composition

Chapter 6 is concerned with the amounts of substances which participate in chemical reactions, the quantities of heat given off or absorbed when reactions occur, and the volumes of solutions which react exactly with one another. These seemingly unrelated subjects are discussed together because many of the calculations involving them are almost identical in form. The same is true of the density calculations, and of the calculations involving molar mass and the Avogadro constant.

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- 6.1: Prelude to Chemical Composition - How Much Sodium?
- 6.2: Counting Nails by the Pound
- 6.3: Counting Atoms by the Gram
- 6.4: Counting Molecules by the Gram
- 6.5: Mass Percent Composition of Compounds
- 6.6: Mass Percent Composition from a Chemical Formula
- 6.7: Calculating Empirical Formulas for Compounds
- 6.8: Calculating Molecular Formulas for Compounds

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6.1: Prelude to Chemical Composition - How Much Sodium?

Why is knowledge of composition important? Everything in nature is either chemically or physically combined with other substances. To find the amount of a material in a sample, you need to know what fraction of the sample it is. Some simple applications of composition are: the amount of sodium in sodium chloride for a diet, the amount of iron in iron ore for steel production, the amount of hydrogen in water for hydrogen fuel, and the amount of chlorine in freon to estimate ozone depletion.



How much salt is in this salt packet? (CC-BY-SA; 3.0; Swilliams).

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6.2: Counting Nails by the Pound

Counting by Weighing and Avogadro's number

The size of molecule is so small that it is physically difficult, if not impossible, to directly count out molecules (Figure 6.2.1). However, we can count them indirectly by using a common trick of "counting by weighing".

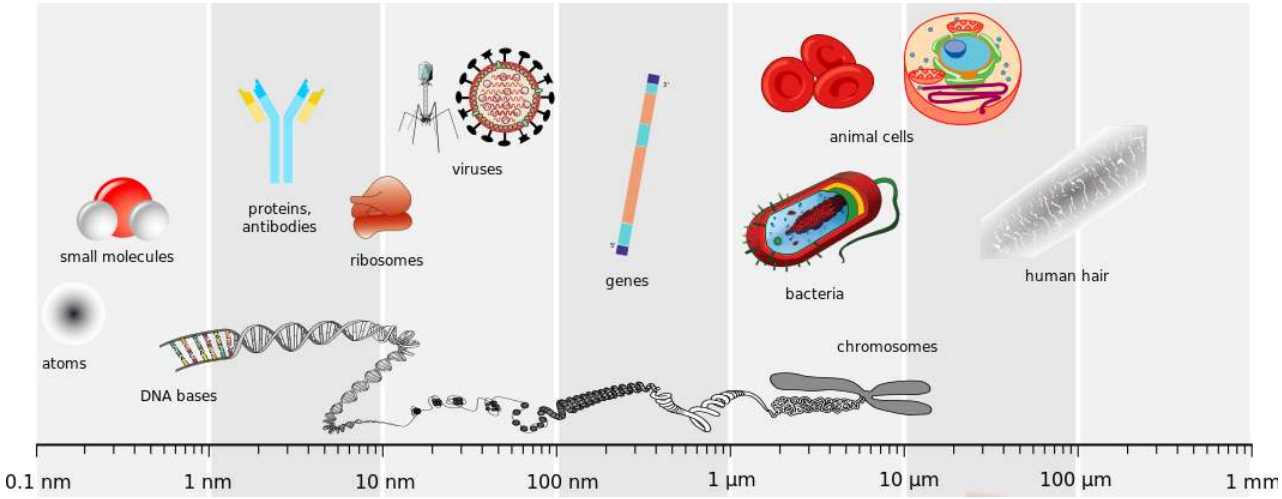


Figure 6.2.1: A comparison of the scales of various biological and technological objects. (CC BY-SA 3.0; Wikipedia)

Consider the example of counting nails in a big box at a hardware store. You need to estimate the number of nails in a box. The weight of an empty box is $213\,g$ and the weight of the box plus a bunch of big nails is $1340\,g$. Assume that we know that the weight of one big nail is 0.450 g. Hopefully it's not necessary to tear open the package and count the nails. We agree that

$$\text{mass of big nails} = 1340\,g - 213\,g = 1227\,g$$

Therefore

$$\text{Number of big nails in box} = \frac{1227\,g}{0.450\,g/\text{big nail}} = 2,726.6\,\text{big nails} = 2,730\,\text{big nails.} \tag{6.2.1}$$

You have just counted the number of big nails in the box by weighing them (rather than by counting them individually).



Figure 6.2.2: Galvanized nails. Individually counting nails in a box would would require significant effort. Alternatively, we can count them by weighing. (Public Domain; Wikipedia).

Now consider if the box of nails weighed the same, but the box were filled with small nails with an individual mass of $0.23\,g/\text{small nail}$ instead? You would do the same math, but use a different denominator in Equation 6.2.1:

$$\text{Number of small nails in box} = \frac{1227\,g}{0.230\,g/\text{small nail}} = 5, \tag{6.2.2}$$
$$334.7\,\text{small nails} = 5,335\,\text{small nails.}$$

The individual mass is the conversion factor used in the calculation and changes, based on the nature of the nail (big or small). Let's ask a different question: how many *dozens* of nails are there in the same box of small nails described above?

If we know the information from Equation 6.2.2, we can just use the conversion of how many nails are in a dozen:

$$\frac{5,335\,\text{small nails}}{12\,\text{small nails/dozen}} = 444.6\,\text{dozen small nails} \tag{6.2.3}$$

If we want to get this value from weighing, we use the "dozen mass" instead of individual mass:

$$12 \times 0.23g = 2.76\,g/\text{dozen small nails.} \tag{6.2.4}$$

So following Equation 6.2.2, we get:

$$\begin{aligned}\text{Number of dozens of small nails} &= \frac{1227\,g}{2.76\,g/\text{dozen small nails}} \\ &= 444.6\,\text{dozen small nails}\end{aligned} \tag{6.2.5}$$

and this is the same result as Equation 6.2.3. These calculations demonstrate the difference between individual mass (i.e., per individual) and collective mass (e.g., per dozen or per gross). The collective mass of most importance to chemistry is *molar mass* (i.e., mass per mole or mass per 6.022×10^{23}).

Avogadro's Number

Avogadro's number is an accident of nature. It is the number of particles that delivers a mole of a substance. Avogadro's number = 6.022×10^{23}. The reason why the value is an accident of nature is that the mole is tied to the gram mass unit. The gram is a convenient mass unit because it matches human sizes. If we were a thousand times greater in size (like Paul Bunyan) we would find it handy to use kilogram amounts. This means the kilogram mole would be convenient. The number of particles handled in a kilogram mole is 1000 times greater. The kilo Avogadro number for the count of particles in a kilomole is 6.022×10^{26}.

If humans were tiny creatures (like Lilliputians) only 1/1000 our present size, milligrams would be more convenient. This means the milligram mole would be more useful. The number of particles handled in a milligram mole (millimole) would be 1/1000 times smaller. The milli Avogadro number for the count of particles in a millimole is 6.022×10^{20}.

What do you think would happen to Avogadro's number if the American system was used and amounts were measured in pound moles? Remember 1 pound = 454 grams. Avogadro's number would be larger by a factor of 454. A pound mole of hydrogen would weigh 1 pound, which is 454 grams. A gram mole of hydrogen weighs 1 gram and contains 6.022×10^{23} H atoms.

Molar Mass for Elements

You are able to read the periodic table and determine the average atomic mass for an element like carbon. The average mass is 12.01 amu. This mass is a ridiculously tiny number of grams. It is too small to handle normally. The molar mass of carbon is defined as the mass in grams that is numerically equal to the average atomic weight. This means

$$1g/molecarbon = 12.01\,g\,carbon$$

this is commonly written

$$1\,mol\,carbon = 12.01\,grams\,carbon.$$

This is the mass of carbon that contains 6.022×10^{23} carbon atoms.

- Avogadro's number is 6.022×10^{23} particles.

This same process gives us the molar mass of any element. For example:

- $1\,mol\,neon = 20.18\,g\,neon\,Ne$
- $1\,mol\,sodium = 22.99\,g\,sodium\,Na$

Molar Mass for Compounds

Example 6.2.1: Molar Mass of Water

The formulas for compounds are familiar to you. You know the formula for water is H_2O. It should be reasonable that the weight of a formula unit can be calculated by adding up the weights for the atoms in the formula.

Solution

The formula weight for water

weight from hydrogen + weight from oxygen

The formula weight for water

2 H atoms x 1.008 amu + 1 O atom x 16.00 amu = 18.016 amu

The molar mass for water

18.016 grams water or 18 grams to the nearest gram

Example 6.2.2: Molar Mass of Methane

The formula for methane, the major component in natural gas, is CH_4.

Solution

The formula weight for methane

weight from hydrogen + weight from carbon

The formula weight for methane

4 H atoms x 1.008 amu + 1 C atom x 12.01 amu = 16.04 amu

The molar mass for methane

16.04 grams per mole of methane

Example 6.2.3: Molar Mass of Ethyl Chloride

What is its molar mass for ethyl chloride CH_3CH_2Cl?

Solution

The *formula weight*

weight from hydrogen + weight from carbon + weight from chlorine

The formula weight

5 H atoms x 1.008 amu + 2 C atom x 12.01 amu + 35.5 amu = 64.5 amu

The molar mass for ethyl chloride

64.5 grams per mole of ethyl chloride

Example 6.2.4: Molar Mass of Sulfur Dioxide

What is the molar mass for sulfur dioxide, $SO_2\,(g)$, a gas used in bleaching and disinfection processes?

Solution

Look up the atomic weight for each of the elements in the formula.

- 1 sulfur atom = 32.07 amu
- 1 oxygen atom = 16.00 amu

Count the atoms of each element in the formula unit.

- one sulfur atom
- two oxygen atoms

The formula weight

weight from sulfur + weight from oxygen

The formula weight

1 sulfur atom x (32. 07 amu) + 2 oxygen atoms x (16.00 amu)

The formula weight

SO_2 = 32. 07 amu + 32.00 amu = 64.07 amu = 64 amu SO_2

The molar mass for SO_2 is

64.07 grams of SO_2; 1 mol SO_2 = 64 grams per mole of SO_2

? Exercise 6.2.1

What is the formula weight and molar mass for alum, $KAl(SO_4)_2 \cdot 12H_2O$?

Answer

1. Check the periodic table for the atomic masses for each atom in the formula.
2. Count the number of each type of atom in the formula.
3. Multiply the number of atoms by the atomic mass for each element.
4. Add up the masses for all of the elements.

Table 6.2.1: Masses of each element in alum, $KAl(SO_4)_2 \cdot 12H_2O$

element	average atomic mass	number of atoms in formula	rounded to nearest one unit for simplicity
potassium k	39.1 amu	1	39. amu
aluminum	26.98 amu	1	27. amu
sulfur	32.07 amu	2	64. amu
oxygen	16.00 amu	8 + 12 = 20	320. amu
hydrogen	1.008 amu	2 x 12 = 24	24. amu

Molar mass is 474 grams (add up the amu of each element to find the total of 474 amu). This is a mass in grams that is numerically (474) the same as the formula weight.

1 mole alum $KAl(SO_4)_2 \cdot 12H_2O$ = 474 grams alum $KAl(SO_4)_2 \cdot 12H_2O$

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6.3: Counting Atoms by the Gram

Learning Objectives

- Use Avogadro's number to convert to moles and vice versa given the number of particles of an element.
- Use the molar mass to convert to grams and vice versa given the number of moles of an element.

When objects are very small, it is often inconvenient, inefficient, or even impossible to deal with the objects one at a time. For these reasons, we often deal with very small objects in groups, and have even invented names for various numbers of objects. The most common of these is "dozen" which refers to 12 objects. We frequently buy objects in groups of 12, like doughnuts or pencils. Even smaller objects such as straight pins or staples are usually sold in boxes of 144, or a dozen dozen. A group of 144 is called a "gross".

This problem of dealing with things that are too small to operate with as single items also occurs in chemistry. Atoms and molecules are too small to see, let alone to count or measure. Chemists needed to select a group of atoms or molecules that would be convenient to operate with.

Avogadro's Number and Mole

In chemistry, it is impossible to deal with a single atom or molecule because we can't see them, count them, or weigh them. Chemists have selected a number of particles with which to work that is convenient. Since molecules are extremely small, you may suspect this number is going to be very large, and you are right. The number of particles in this group is $\mathbf{6.02 \times 10^{23}}$ particles and the name of this group is the **mole** (the abbreviation for ***mole*** is $\mathbf{mol}$). One mole of any object is $\mathbf{6.02 \times 10^{23}}$ of those objects. There is a particular reason that this number was chosen and this reason will become clear as we proceed.

When chemists are carrying out chemical reactions, it is important that the relationship between the numbers of particles of each reactant is known. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extremely large numerical unit is needed to count them. The mole is used for this purpose.

The **mole** (symbol: **mol**) is the base unit of amount of substance ("number of substance") in the International System of Units or System International (SI), defined as exactly 6.02214076×10^{23} particles, e.g., atoms, molecules, ions or electrons. The current definition was adopted in November 2018, revising its old definition based on the number of atoms in 12 grams of carbon-12 (^{12}C) (the isotope of carbon with relative atomic mass 12 Daltons, by definition). For most purposes, 6.022×10^{23} provides an adequate number of significant figures. Just as 1 mole of atoms contains 6.022×10^{23} atoms, 1 mole of eggs contains 6.022×10^{23} eggs. This number is called Avogadro's number, after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain.

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that 1 mole of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23}.

Converting Between Number of Atoms to Moles and Vice Versa

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

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

Example 6.3.1: Moles of Carbon

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

Solution

Solutions to Example 6.3.1

Steps for Problem Solving	The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.72×10^{24} C atoms Find: mol C
List other known quantities.	$1\,mol = 6.022 \times 10^{23}$ C atoms
Prepare a concept map and use the proper conversion factor.	# C atoms → mol C $\frac{1\ mol\ C}{6.022 \times 10^{23} C\ atoms}$
Cancel units and calculate.	$4.72 \times 10^{24}\ \cancel{\text{C atoms}} \times \frac{1\ \text{mol C}}{6.02 \times 10^{23}\ \cancel{\text{C atoms}}} = 7.84\ \text{mol C}$
Think about your result.	The given number of carbon atoms was greater than Avogadro's number, so the number of moles of C atoms is greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded to three significant figures.

Molar Mass

Molar mass is defined as the mass of one mole of representative particles of a substance. By looking at a periodic table, we can conclude that the molar mass of the element lithium is 6.94g, the molar mass of zinc is 65.38g, and the molar mass of gold is 196.97g. Each of these quantities contains 6.022×10^{23} atoms of that particular element. The units for molar mass are grams per mole or g/mol. $1.00\ \text{mol}$ of carbon-12 atoms has a mass of $12.0\ \text{g}$ and contains 6.022×10^{23} atoms. 1.00 mole of any element has a mass numerically equal to its atomic mass in grams and contains 6.022×10^{23} particles. The mass, in grams, of 1 mole of particles of a substance is now called the **molar mass** (mass of 1.00 mole).

Converting Grams to Moles of an Element and Vice Versa

We can also convert back and forth between grams of an element and moles. The conversion factor for this is the molar mass of the substance. The **molar mass** is the ratio giving the number of grams for each one mole of the substance. This ratio is easily found by referring to the atomic mass of the element using the periodic table. This ratio has units of grams per mole or g/mol.

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 6.4.1 illustrates what conversion factor is needed and two examples are given below.

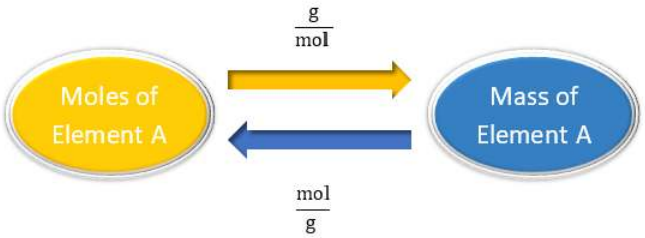


Figure **6.3.1**: A Simple Flowchart for Converting Between Mass and Moles of an Element.
Flowchart: to convert moles of Element A to mass of Element A, use g/mol, and to convert vice versa, use mol/g.

Example 6.3.2: Chromium

Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.

Solution

Solutions to Example 6.3.2

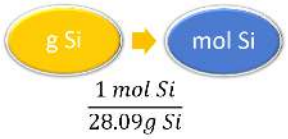
Steps for Problem Solving	**Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.**
Identify the "given" information and what the problem is asking you to "find."	Given: 0.560 mol Cr Find: g Cr
List other known quantities.	1 mol Cr = 52.00g Cr
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$0.560\ \cancel{\text{mol Cr}} \times \frac{52.00\ \text{g Cr}}{1\ \cancel{\text{mol Cr}}} = 29.1\ \text{g Cr}$
Think about your result.	Since the desired amount was slightly more than one half of a mole, the mass should be slightly more than one half of the molar mass. The answer has three significant figures because of the **0.560 mol**

Example 6.3.3: Silicon

How many moles are in 107.6g of Si?

Solution

Solutions to Example 6.3.3

Steps for Problem Solving	**How many moles are in 107.6g of Si.**
Identify the "given" information and what the problem is asking you to "find."	Given: 107.6g Si Find: mol Si
List other known quantities.	1 mol Si = 28.09g Si
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$107.6\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 3.83\ \text{mol Si}$
Think about your result.	Since 1 mol of Si is 28.09g, 107.6 should be about 4 moles.

? Exercise 6.3.1

a. How many moles are present in 100.0 g of Al?
b. What is the mass of 0.552 mol of Ag metal?

Answer a:

3.706 mol Al

Answer b:

59.5 g Ag

Summary

- A mole is defined as exactly $6.02214076 \times 10^{23}$ particles, e.g., atoms, molecules, ions or electrons.
- There are $\mathbf{6.02214076 \times 10^{23}}$ particles in 1.00 mole. This number is called Avogadro's number.
- The molar mass of an element can be found by referring to the atomic mass on a periodic table with units of g/mol.
- Using dimensional analysis, it is possible to convert between grams, moles, and the number of atoms or molecules.

Further Reading/Supplemental Links

- learner.org/resources/series61.html - The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos, but there is no charge. The website has one video that relates to this lesson called ***The Mole***.
- Using Avogadro's law, the mass of a substance can be related to the number of particles contained in that mass. The Mole: (www.learner.org/vod/vod_window.html?pid=803)
- Vision Learning tutorial: The Mole http://visionlearning.com/library/mo...p?mid-53&1=&c3=

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6.4: Counting Molecules by the Gram

Learning Objectives

- Define molecular mass and formula mass.
- Perform conversions between mass and moles of a compound.
- Perform conversions between mass and number of particles.

Molecular and Formula Masses

The molecular mass of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example **6.4.1**.

Example 6.4.1: Ethanol

Calculate the molecular mass of ethanol, whose condensed structural formula is $\mathbf{CH_3CH_2OH}$. Among its many uses, ethanol is a fuel for internal combustion engines

Solution

Solutions to Example 6.4.1

Steps for Problem Solving	Calculate the molecular mass of ethanol, whose condensed structural formula is $\mathbf{CH_3CH_2OH}$
Identify the "given"information and what the problem is asking you to "find."	Given: Ethanol molecule (CH_3CH_2OH) Find: molecular mass
Determine the number of atoms of each element in the molecule.	The molecular formula of ethanol may be written in three different ways: • CH_3CH_2OH (which illustrates the presence of an ethyl group • CH_3CH_2–, and an −OH group) • C_2H_5OH, and C_2H_6O; All show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.
Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.	1 C atom = 12.011 amu 1 H atom = 1.0079 amu 1 O atom = 15.9994 amu
Add the masses together to obtain the molecular mass.	2C: (2 atoms)(12.011amu/atom) = 24.022 amu 6H: (6 atoms)(1.0079amu/atom) = 6.0474amu +1O: (1 atoms)(15.9994amu/atom) =15.9994amu C_2H_6O : molecular mass of ethanol = 46.069amu

Exercise 6.4.1: Freon

Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, which has a condensed structural formula of $\mathbf{CCl_3F}$. Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:

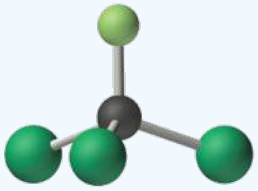


Figure 6.4.1: Molecular structure of freon-11, CCl_3F.

Answer

137.37 amu

Unlike molecules, which form covalent bonds, ionic compounds do not have a readily identifiable molecular unit. Therefore, for ionic compounds, the **formula mass** (also called the empirical formula mass) of the compound is used instead of the molecular mass. The formula mass is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. The units are atomic mass units.

> *Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.*

Example 6.4.2: Calcium Phosphate

Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

Solution

Solutions to Example 6.4.2

Steps for Problem Solving	Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate.
Identify the "given" information and what the problem is asking you to "find."	Given: Calcium phosphate [$Ca_3(PO_4)_2$] formula unit Find: formula mass
Determine the number of atoms of each element in the molecule.	• The empirical formula—$Ca_3(PO_4)_2$—indicates that the simplest electrically neutral unit of calcium phosphate contains three Ca^{2+} ions and two PO_4^{3-} ions. • The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.
Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.	1 Ca atom = 40.078 amu 1 P atom = 30.973761 amu 1 O atom = 15.9994 amu
Add together the masses to give the formula mass.	3Ca: (3 atoms) (40.078 amu/atom)=120.234amu 2P: (2 atoms) (30.973761amu/atom)=61.947522amu + 8O: (8 atoms)(15.9994amu/atom)=127.9952amu Formula mass of $Ca_3(PO_4)_2$=310.177amu

Exercise 6.4.2: Silicon Nitride

Calculate the formula mass of Si_3N_4, commonly called silicon nitride. It is an extremely hard and inert material that is used to make cutting tools for machining hard metal alloys.



Figure 6.4.2: Si_3N_4 bearing parts. (Public Domain; David W. Richerson and Douglas W. Freitag; Oak Ridge National Laboratory).

Answer

140.29 amu

Molar Mass

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

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

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

Table 6.4.1: Molar Mass of Select Substances

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

Converting Between Grams and Moles of a Compound

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment you need 3.00 moles of calcium chloride ($CaCl_2$). Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure as shown in Example 6.4.3.

Example 6.4.3: Calcium Chloride

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



Figure **6.4.3**: Calcium chloride is used as a drying agent and as a road deicer.

Solution

Solutions to Example 6.4.3

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

Exercise **6.4.3**: Calcium Oxide

What is the mass of $\mathbf{7.50\ mol}$ of (calcium oxide) $\mathbf{CaO}$?

Answer

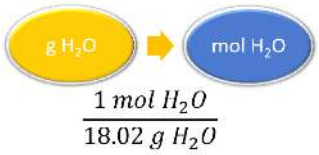
420.60 g

Example **6.4.4**: Water

How many moles are present in 108 grams of water?

Solution

Solutions to Example 6.4.4

Steps for Problem Solving	How many moles are present in 108 grams of water?
Identify the "given" information and what the problem is asking you to "find."	Given: 108 g $\mathbf{H_2O}$ Find: mol $\mathbf{H_2O}$
List other known quantities.	$\mathbf{1\ mol\ H_2O = 18.02\ g}$ H2O
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$\mathbf{108\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} = 5.99\ mol\ H_2O}$
Think about your result.	

? Exercise 6.4.4: Nitrogen Gas

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

Answer

210 g

Conversions Between Mass and Number of Particles

In "Conversions Between Moles and Mass", you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to moles. To convert from mass to number of particles or vice-versa, it will first require a conversion to moles as shown in Figure 6.4.1 and Example 6.4.5.

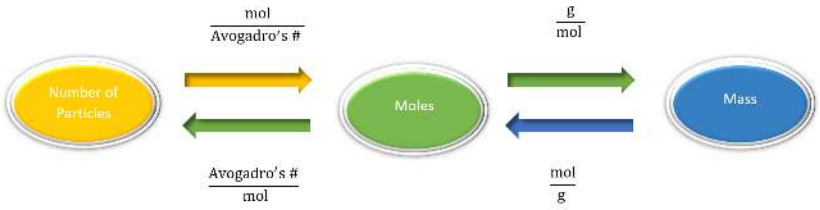


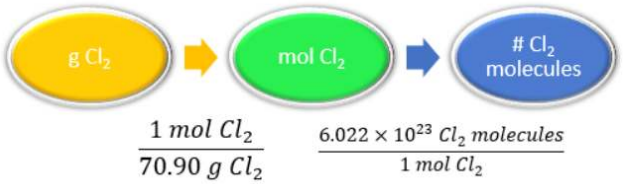
Figure 6.4.4: Conversion from number of particles to mass, or from mass to number of particles, requires two steps. To convert from number of particles to moles, use mol/Avogrado's #, an d to convert from moles to mass, use g/mol.

✓ Example 6.4.5: Chlorine

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

Solution

Solutions to Example 6.4.5

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

? Exercise 6.4.5: Calcium Chloride

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

Answer

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

Summary

- Calculations for formula mass and molecular mass are described.
- Calculations involving conversions between moles of a material and the mass of that material are described.
- Calculations are illustrated for conversions between mass and number of particles.

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6.5: Mass Percent Composition of Compounds

Learning Objectives

- Determine percent composition of each element in a compound based on mass.

Packaged foods that you eat typically have nutritional information provided on the label. The label on a jar of peanut butter reveals that one serving size is considered to be **32 g**. The label also gives the masses of various types of compounds that are present in each serving. One serving contains **7 g** of protein, **15 g** of fat, and **3 g** of sugar. By calculating the fraction of protein, fat, or sugar in one serving size of peanut butter and converting to percent values, we can determine the composition of peanut butter on a percent by mass basis.

Percent Composition

Chemists often need to know what elements are present in a compound and in what percentage. The **percent composition** is the percent by mass of each element in a compound. It is calculated in a similar way to that of the composition of the peanut butter.

$$\%\text{ by mass} = \frac{\text{mass of element}}{\text{mass of compound}} \times 100\%$$

The sample problem below shows the calculation of the percent composition of a compound based on mass data.

Example 6.5.1: Percent Composition from Mass Data

A certain newly synthesized compound is known to contain the elements zinc and oxygen. When a **20.00 g** sample of the compound is decomposed, **16.07 g** of zinc remains. Determine the percent composition of the compound.

Solution

Solutions to Example 6.6.1

Steps for Problem Solving	When a 20.00 g sample of the zinc-and-oxygen compound is decomposed, 16.07 g of zinc remains. Determine the percent composition of the compound.
Identify the "given" information and what the problem is asking you to "find."	Given : Mass of compound = 20.00 g Mass of Zn = 16.07 g Find: % Composition (% Zn and %O)
List other known quantities.	Subtract to find the mass of oxygen in the compound. Divide each element's mass by the mass of the compound to find the percent by mass. Mass of oxygen = 20.00 g - 16.07 g = 3.93 g O
Cancel units and calculate.	$\%\text{ Zn} = \frac{16.07\text{ g Zn}}{20.00\text{ g}} \times 100\% = 80.35\%\text{ Zn}$ $\%\text{ O} = \frac{3.93\text{ g O}}{20.00\text{ g}} \times 100\% = 19.65\%\text{ O}$ Calculate the percent by mass of each element by dividing the mass of that element by the mass of the compound and multiplying by **100%**.
Think about your result.	The calculations make sense because the sum of the two percentages adds up to **100%**. By mass, the compound is mostly zinc.

? Exercise 6.5.1

Sulfuric acid, H_2SO_4 is a very useful chemical in industrial processes. If 196.0 g of sulfuric acid contained 64.0g oxygen and 4.0 g of hydrogen, what is the percent composition of the compound?

Answer

2.04% H, 32.65% S, and 65.3% O

Summary

- Processes are described for calculating the percent composition of a compound based on mass.

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6.6: Mass Percent Composition from a Chemical Formula

Learning Objectives

- Determine the percent composition of each element in a compound from the chemical formula.

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. This is divided by the molar mass of the compound and multiplied by 100%.

$$\%\text{ by mass} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same, given that the compound is pure.

Example 6.6.1

Dichlorine heptoxide (Cl_2O_7) is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorine heptoxide.

Solution

Solutions to Example 6.7.1

Steps for Problem Solving	**Calculate the percent composition of dichlorine heptoxide (Cl_2O_7).**
Identify the "given" information and what the problem is asking you to "find."	Given : Cl_2O_7 Find: % Composition (% Cl and %O)
List other known quantities.	Mass of Cl in 1 mol Cl_2O_7 , 2 Cl : 2 x 35.45 g = 70.90 g Mass of O in 1 mol Cl_2O_7 , 7 O: 7 x 16.00 g = 112.00 g Molar mass of Cl_2O_7 = 182.90 g/mol
Cancel units and calculate.	$$\%Cl = \frac{70.90\text{ g Cl}}{182.90\text{ g}} \times 100\% = 38.76\%\text{ Cl}$$ $$\%\text{ O} = \frac{112.00\text{ g O}}{182.90\text{ g}} \times 100\% = 61.24\%\text{ O}$$ Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%.
Think about your result.	The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is 38.76% Cl and 61.24% O. Suppose that you needed to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element.

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

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

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

? Exercise 6.6.1

Barium fluoride is a transparent crystal that can be found in nature as the mineral frankdicksonite. Determine the percent composition of barium fluoride.

Answer a:

78.32% Ba and 21.67% F

Summary

- Processes are described for calculating the percent composition of a compound based on the chemical formula.

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6.7: Calculating Empirical Formulas for Compounds

Learning Objectives

- Define empirical formula.
- Determine empirical formula from percent composition of a compound.

In the early days of chemistry, there were few tools for the detailed study of compounds. Much of the information regarding the composition of compounds came from the elemental analysis of inorganic materials. The "new" field of organic chemistry (the study of carbon compounds) faced the challenge of not being able to characterize a compound completely. The relative amounts of elements could be determined, but so many of these materials had carbon, hydrogen, oxygen, and possibly nitrogen in simple ratios. We did not know exactly how many of these atoms were actually in a specific molecule.

Determining Empirical Formulas

An empirical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O** is composed **of 2.0 moles of hydrogen** and **1.0 mole of oxygen**. We can also work backwards from molar ratios because *if we know the molar amounts of each element in a compound, we can determine the empirical formula.*

> *In a procedure called elemental analysis, an unknown compound can be analyzed in the laboratory in order to determine the percentages of each element contained within it. These percentages can be transformed into the mole ratio of the elements, which leads to the empirical formula.*

Empirical Formula: In Steps

Steps to determine empirical formula:

1. Assume a **100 g** sample of the compound so that the given percentages can be directly converted into grams.
2. Use each element's molar mass to convert the grams of each element to moles.
3. In order to find a whole-number ratio, divide the moles of each element by whichever of the moles from step 2 is the smallest.
4. If all the moles at this point are whole numbers (or very close), the empirical formula can be written with the moles as the subscript of each element.
5. In some cases, one or more of the moles calculated in step 3 will not be whole numbers. Multiply each of the moles by the smallest whole number that will convert each into a whole number. Write the empirical formula.

Example 6.7.1

A compound of iron and oxygen is analyzed and found to contain **69.94%** iron and **30.06%** oxygen. Find the empirical formula of the compound.

Solution

Solutions to Example 6.8.1

Steps for Problem Solving	**Find the empirical formula of a compound of 69.94% iron and 30.06% oxygen.**
Identify the "given" information and what the problem is asking you to "find."	Given: % of $\mathrm{Fe} = 69.94\%$ % of $\mathrm{O} = 30.06\%$ Find: Empirical formula $= \mathrm{Fe_?O_?}$
Calculate	
a. Assume a $100\ \mathrm{g}$ sample, convert the same % values to grams.	$69.94\ \mathrm{g\ Fe}$ $30.06\ \mathrm{g\ O}$
b. Convert to moles.	$69.94\ \mathrm{g\ Fe} \times \frac{1\ \mathrm{mol\ Fe}}{55.85\ \mathrm{g\ Fe}} = 1.252\ \mathrm{mol\ Fe}$ $30.06\ \mathrm{g\ O} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g\ O}} = 1.879\ \mathrm{mol\ O}$
c. Divide both moles by the smallest of the results.	$\mathrm{Fe}: \frac{1.252\ \mathrm{mol}}{1.252}$ $\mathrm{O}: \frac{1.879\ \mathrm{mol}}{1.252}$ The "non-whole number" empirical formula of the compound is $\mathrm{Fe_1O_{1.5}}$
Multiply each of the moles by the smallest whole number that will convert each into a whole number.	Fe:O = 2 (1:1.5) = 2:3 Since the moles of O is still not a whole number, both moles can be multiplied by 2, while rounding to a whole number.
Write the empirical formula.	The empirical formula of the compound is $\mathrm{Fe_2O_3}$.
Think about your result.	The subscripts are whole numbers and represent the mole ratio of the elements in the compound. The compound is the ionic compound iron (III) oxide.

? Exercise 6.7.1

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Answer

$\mathrm{HgCl_2}$

Summary

- A process is described for the calculation of the empirical formula of a compound, based on the percent composition of that compound.

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6.8: Calculating Molecular Formulas for Compounds

Learning Objectives

- Understand the difference between empirical formulas and molecular formulas.
- Determine molecular formula from percent composition and molar mass of a compound.

Below, we see two carbohydrates: glucose and sucrose. Sucrose is almost exactly twice the size of glucose, although their empirical formulas are very similar. Some people can distinguish them on the basis of taste, but it's not a good idea to go around tasting chemicals. The best way to tell glucose and sucrose apart is to determine the molar masses—this approach allows you to easily tell which compound is which.

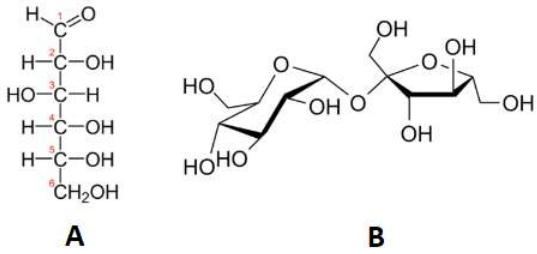


Figure 6.8.1: (A) the molecular structure of glucose and (B) the molecular structure of sucrose.

Molecular Formulas

Molecular formulas give the kind and number of atoms of each element present in the molecular compound. In many cases, the molecular formula is the same as the empirical formula. The chemical formula will always be some *integer multiple* (n) of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula).

$$\text{Molecular Formula} = n(\text{Empirical formula})$$

therefore

$$n = \frac{\text{Molecular Formula}}{\text{Empirical Formula}}$$

The integer multiple, n, can also be obtained by dividing the molar mass, MM, of the compound by the empirical formula mass, EFM (the molar mass represented by the empirical formula).

$$n = \frac{MM(molar mass)}{EFM(empirical formula molar mass)}$$

Table 6.8.1 shows the comparison between the empirical and molecular formula of methane, acetic acid, and glucose, and the different values of n. The molecular formula of methane is CH_4 and because it contains only one carbon atom, that is also its empirical formula. Sometimes, however, the molecular formula is a simple whole number multiple of the empirical formula. Acetic acid is an organic acid that is the main component of vinegar. Its molecular formula is $C_2H_4O_2$. Glucose is a simple sugar that cells use as a primary source of energy. Its molecular formula is $C_6H_{12}O_6$. The structures of both molecules are shown in Figure 6.8.2. They are very different compounds, yet both have the same empirical formula of CH_2O.

Table 6.8.1: Molecular Formula and Empirical Formula of Various Compounds.

Name of Compound	Molecular Formula	Empirical Formula	n
Methane	CH_4	CH_4	1
Acetic acid	$C_2H_4O_2$	CH_2O	2
Glucose	$C_6H_{12}O_6$	CH_2O	6

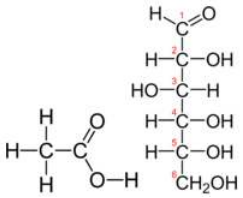


Figure 6.8.2: Acetic acid (left) has a molecular formula of $C_2H_4O_2$, while glucose (right) has a molecular formula of $C_6H_{12}O_6$. Both have the empirical formula CH_2O.

Empirical formulas can be determined from the percent composition of a compound as discussed in section 6.8. In order to determine its molecular formula, it is necessary to know the molar mass of the compound. Chemists use an instrument called a mass spectrometer to determine the molar mass of compounds. In order to go from the empirical formula to the molecular formula, follow these steps:

1. Calculate the **empirical formula molar mass (EFM)**.
2. Divide the molar mass of the compound by the empirical formula molar mass. The result should be a whole number or very close to a whole number.
3. Multiply all the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.

✔ Example 6.8.1

The empirical formula of a compound of boron and hydrogen is BH_3. Its molar mass is $27.7\ g/mol$. Determine the molecular formula of the compound.

Solution

Solutions to Example 6.9.1

Steps for Problem Solving	Determine the molecular formula of BH_3.
Identify the "given" information and what the problem is asking you to "find."	Given: Empirical formula $= BH_3$ Molar mass $= 27.7\ g/mol$ Find: Molecular formula $=?$
Calculate the empirical formula mass (EFM).	$\text{Empirical formula molar mass (EFM)} = 13.84\ g/mol$
Divide the molar mass of the compound by the empirical formula mass. The result should be a whole number or very close to a whole number.	$\frac{\text{molar mass}}{\text{EFM}} = \frac{27.7 g/mol}{13.84 g/mol} = 2$
Multiply all the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.	$BH_3 \times 2 = B_2H_6$
Write the molecular formula.	The molecular formula of the compound is B_2H_6.
Think about your result.	The molar mass of the molecular formula matches the molar mass of the compound.

? Exercise 6.8.1

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What are the empirical and chemical formulas for ascorbic acid?

Answer Empirical Formula

$C_3H_4O_3$

Answer Molecular Formula

$C_6H_8O_6$

Summary

- A procedure is described that allows the calculation of the exact molecular formula for a compound.

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CHAPTER OVERVIEW

7: Chemical Reactions

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7.1: Prelude to Chemical Reactions
7.2: Evidence of a Chemical Reaction
7.3: Chemical Equations
7.4: How to Write Balanced Chemical Equations
7.5: Acid–Base and Gas Evolution Reactions
7.6: Oxidation–Reduction Reactions
7.7: Classifying Chemical Reactions

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7.1: Prelude to Chemical Reactions

The space shuttle—and any other rocket-based system—uses chemical reactions to propel itself into space and maneuver itself when it gets into orbit. The rockets that lift the orbiter are of two different types. The three main engines are powered by reacting liquid hydrogen with liquid oxygen to generate water. Then there are the two solid rocket boosters, which use a solid fuel mixture that contains mainly ammonium perchlorate and powdered aluminum. The chemical reaction between these substances produces aluminum oxide, water, nitrogen gas, and hydrogen chloride. Although the solid rocket boosters each have a significantly lower mass than the liquid oxygen and liquid hydrogen tanks, they provide over 80% of the lift needed to put the shuttle into orbit—all because of chemical reactions.



Figure **7.1.1** The Space Shuttle. (Public Domain; NASA).

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7.2: Evidence of a Chemical Reaction

Learning Objectives

- Identify the evidence for chemical reactions.

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

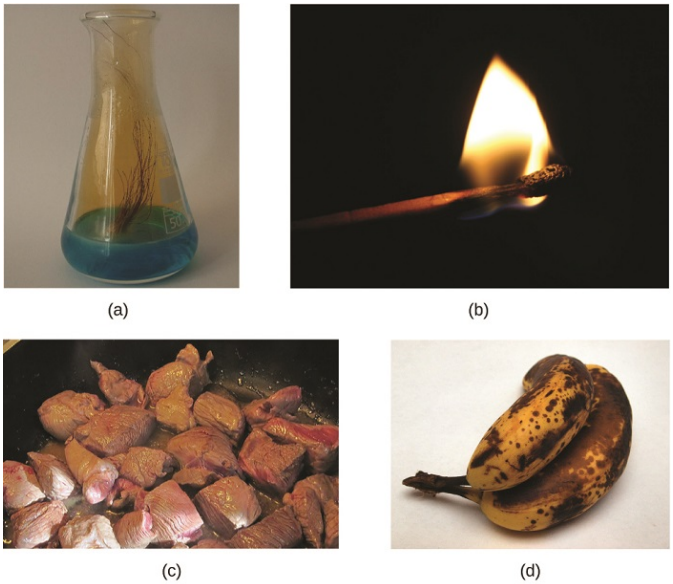


Figure **7.2.1**: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (Credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo.)

To identify a chemical reaction, we look for a **chemical change**. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include: reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure **7.2.1**).



***Video*7.2.1*:** *Evidence of a Chemical Reaction*

Example 7.2.1: Evidence of a Chemical Reaction

Which of the following is a chemical reaction?

a. Freezing liquid mercury.
b. Adding yellow to blue to make green.
c. Cutting a piece of paper into two pieces.
d. Dropping a sliced orange into a vat of sodium dydroxide.
e. Filling a balloon with natural air.

Solution

A, B, C, & E involve only physical changes. A sliced orange has acid (citric acid) that can react with sodium hydroxide, so the answer is D.

Exercise 7.2.1

Which of the following is a chemical reaction?

a. Painting a wall blue.
b. A bicycle rusting.
c. Ice cream melting.
d. Scratching a key across a desk.
e. Making a sand castle.

Answer

B

Example 7.2.2: Evidence of a Chemical Reaction

Which of the following is not a chemical reaction?

a. Shattering glass with a baseball.
b. Corroding metal.
c. Fireworks exploding.
d. Lighting a match.
e. Baking a cake.

Solution

Shattering glass with a baseball results in glass broken into many pieces but no chemical change happens, so the answer is A.

? Exercise 7.2.2

Which of the following is NOT a chemical reaction?

a. Frying an egg.
b. Slicing carrots.
c. A Macbook falling out of a window.
d. Creating ATP in the human body.
e. Dropping a fizzy tablet into a glass of water.

Answer

B and C

Summary

Chemical reactions can be identified via a wide range of different observable factors including change in color, energy change (temperature change or light produced), gas production, formation of precipitate and change in properties.

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7.3: Chemical Equations

Learning Objectives

- Identify the reactants and products in any chemical reaction.
- Convert word equations into chemical equations.
- Use the common symbols, (s), (l), (g), (aq), and $\rightarrow$ appropriately when writing a chemical reaction.

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

Reactants and Products

To describe a chemical reaction, we need to indicate what substances are present at the beginning and what substances are present at the end. The substances that are present at the beginning are called **reactants** and the substances present at the end are called **products**.

Sometimes when reactants are put into a reaction vessel, a reaction will take place to produce products. Reactants are the starting materials, that is, whatever we have as our initial ingredients. The products are just that—what is produced—or the result of what happens to the reactants when we put them together in the reaction vessel. If we think about baking chocolate chip cookies, our reactants would be flour, butter, sugar, vanilla, baking soda, salt, egg, and chocolate chips. What would be the products? Cookies! The reaction vessel would be our mixing bowl.

$$\underbrace{\text{Flour}+\text{Butter}+\text{Sugar}+\text{Vanilla}+\text{Baking Soda}+\text{Eggs}+\text{Chocolate Chips}}_{\text{Ingredients = Reactants}} \rightarrow \underbrace{\text{Cookies}}_{\text{Product}}$$

Writing Chemical Equations

When sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen, $SO_2 + O_2$, are reactants and sulfur trioxide, SO_3, is the product.

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

In chemical reactions, the reactants are found before the symbol "$\rightarrow$" and the products are found after the symbol "$\rightarrow$". The general equation for a reaction is:

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

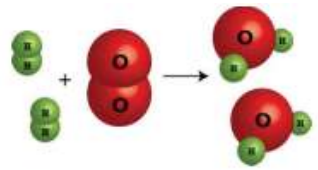
There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. Table **7.3.1** shows a listing of symbols used in chemical equations.

Table **7.3.1**: Symbols Used in Chemical Equations

Symbol	Description	Symbol	Description
$+$	used to separate multiple reactants or products	(s)	reactant or product in the solid state
$\rightarrow$	yield sign; separates reactants from products	(l)	reactant or product in the liquid state
$\rightleftharpoons$	replaces the yield sign for reversible reactions that reach equilibrium	(g)	reactant or product in the gas state
$\xrightarrow{\text{Pt}}$	formula written above the arrow is used as a catalyst in the reaction	(aq)	reactant or product in an aqueous solution (dissolved in water)
$\xrightarrow{\Delta}$	triangle indicates that the reaction is being heated		

Chemists have a choice of methods for describing a chemical reaction.

1. They could draw a picture of the chemical reaction.



2. They could write a word equation for the chemical reaction:
"Two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water vapor."

3. They could write the equation in chemical shorthand.

$$2\text{H}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{H}_2\text{O}\,(g)$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products, while symbols are used to indicate the phase of each substance. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

We could write that an aqueous solution of calcium nitrate is added to an aqueous solution of sodium hydroxide to produce solid calcium hydroxide and an aqueous solution of sodium nitrate. Or in shorthand we could write:

$$\text{Ca}(\text{NO}_3)_2\,(aq) + 2\text{NaOH}\,(aq) \rightarrow \text{Ca}(\text{OH})_2\,(s) + 2\text{NaNO}_3\,(aq)$$

How much easier is that to read? Let's try it in reverse. Look at the following reaction in shorthand and write the word equation for the reaction:

$$\text{Cu}\,(s) + \text{AgNO}_3\,(aq) \rightarrow \text{Cu}(\text{NO}_3)_2\,(aq) + \text{Ag}\,(s)$$

The word equation for this reaction might read something like "solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver."

To turn word equations into symbolic equations, we need to follow the given steps:

1. Identify the reactants and products. This will help you know which symbols go on each side of the arrow and where the $+$ signs go.
2. Write the correct formulas for all compounds. You will need to use the rules you learned in Chapter 5 (including making all ionic compounds charge balanced).

3. Write the correct formulas for all elements. Usually this is given straight off of the periodic table. However, there are seven elements that are considered diatomic, meaning that they are always found in pairs in nature. They include those elements listed in the table.

Table **7.3.1**: *Diatomic Elements*

Element Name	Hydrogen	Nitrogen	Oxygen	Fluorine	Chlorine	Bromine	Iodine
Formula	H_2	N_2	O_2	F_2	Cl_2	Br_2	I_2

Example 7.3.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. $\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$

b. Gaseous propane, $\mathrm{C_3H_8}$, burns in oxygen gas to produce gaseous carbon dioxide and liquid water.

c. Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

Solution

a. An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

b. Reactants: propane ($\mathrm{C_3H_8}$) and oxygen ($\mathrm{O_2}$)

Product: carbon dioxide ($\mathrm{CO_2}$) and water ($\mathrm{H_2O}$)

$$\mathrm{C_3H_8}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

$$\mathrm{HF}\,(g) + \mathrm{K_2CO_3}\,(aq) \rightarrow \mathrm{KF}\,(aq) + \mathrm{H_2O}\,(l) + \mathrm{CO_2}\,(g)$$

Exercise 7.3.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. Hydrogen gas reacts with nitrogen gas to produce gaseous ammonia.

b. $\mathrm{HCl}\,(aq) + \mathrm{LiOH}\,(aq) \rightarrow \mathrm{LiCl}\,(aq) + \mathrm{H_2O}\,(l)$

c. Copper metal is heated with oxygen gas to produce solid copper(II) oxide.

Answer a

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

Answer b

An aqueous solution of hydrochloric acid reacts with an aqueous solution of lithium hydroxide to produce an aqueous solution of lithium chloride and liquid water.

Answer c

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

Summary

- A chemical reaction is the process by which one or more substances are changed into one or more new substances.
- Chemical reactions are represented by chemical equations.
- Chemical equations have reactants on the left, an arrow that is read as "yields", and the products on the right.

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7.4: How to Write Balanced Chemical Equations

Learning Objectives

- Explain the roles of subscripts and coefficients in chemical equations.
- Balance a chemical equation when given the unbalanced equation.
- Explain the role of the Law of Conservation of Mass in a chemical reaction.

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear, nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products—they are merely reorganized into different arrangements. In a complete chemical equation, the two sides of the equation must be present on the reactant and the product sides of the equation.

Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products; and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

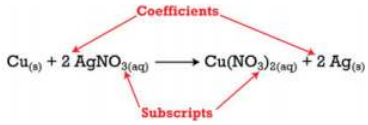
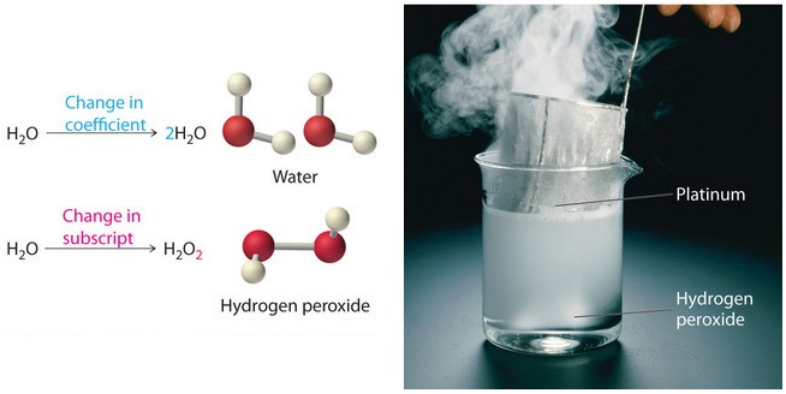


Figure **7.4.1**: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

Balancing a Chemical Equation

Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure **7.4.1**.



Original molecule $\mathbf{H_2O}$: if the coefficient 2 is added in front, that makes 2 water molecules; but if the subscript 2 is added to make $\mathbf{H_2O_2}$, that's hydrogen peroxide.

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element(s) that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element(s) on both sides.
3. Balance polyatomic ions (if present on both sides of the chemical equation) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example 7.4.1: Combustion of Heptane

Balance the chemical equation for the combustion of Heptane (C_7H_{16}).

$$C_7H_{16}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

Solution

Solutions to Example **7.4.1**

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side: $$C_7H_{16}(l) + O_2(g) \longrightarrow \underline{7}CO_2(g) + H_2O(g)$$ • 7 carbon atoms on both reactant and product sides b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side: $$C_7H_{16}(l) + O_2(g) \longrightarrow 7\,CO_2(g) + \underline{8}H_2O(g)$$ • 16 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side: $$C_7H_{16}(l) + \underline{11}O_2(g) \longrightarrow 7\,CO_2(g) + 8\,H_2O(g)$$ • 22 oxygen atoms on both reactant and product sides
5. **Check your work.**	The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.

Example 7.4.2: Combustion of Isooctane

Combustion of Isooctane (C_8H_{18})

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

Solution

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Solutions to Example 7.4.2

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_8H_{18}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$ • 8 carbon atoms on both reactant and product sides b. 18 hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$ • 18 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2\ (g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ • 25 oxygen atoms on both reactant and product sides The equation is now balanced, but we usually write equations with whole number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by **2**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$
5. **Check your work.**	The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side. Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example 7.4.3: Precipitation of Lead (II) Chloride

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Solutions to Example 7.4.3

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is lead (II) chloride. $\mathrm{Pb(NO_3)_2\,(aq) + NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$
2. **Adjust the coefficients.**	There are twice as many chloride ions in the reactants as there are in the products. Place a 2 in front of the NaCl in order to balance the chloride ions. $\mathrm{Pb(NO_3)_2\,(aq) + \underline{2}\,NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on reactant side, 1 Na atom on product side • 2 Cl atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	The nitrate ions are still unbalanced. Place a 2 in front of the $NaNO_3$. The result is: $\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow \underline{2}\,NaNO_3\,(aq) + PbCl_2\,(s)}$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides
4. **Balance the remaining atoms.**	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow 2\,NaNO_3\,(aq) + PbCl_2\,(s)}$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides

? Exercise 7.4.1

Is each chemical equation balanced?

a. $\mathrm{2\,Hg(\ell) + O_2\,(g) \rightarrow Hg_2O_2\,(s)}$
b. $\mathrm{C_2H_4\,(g) + 2\,O_2(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(g)}$
c. $\mathrm{Mg(NO_3)_2\,(s) + 2\,Li\,(s) \rightarrow Mg(s) + 2\,LiNO_3\,(s)}$

Answer a

yes

Answer b

no

Answer c

yes

Exercise 7.4.2

Balance the following chemical equations.

a. $\mathbf{N_2\,(g) + O_2\,(g) \longrightarrow NO_2\,(g)}$
b. $\mathbf{Pb(NO_3)_2\,(aq) + FeCl_3\,(aq) \longrightarrow Fe(NO_3)_3\,(aq) + PbCl_2\,(s)}$
c. $\mathbf{C_6H_{14}\,(l) + O_2(g) \longrightarrow CO_2\,(g) + H_2O\,(g)}$

Answer a

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

Answer b

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

Answer c

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

Summary

- To be useful, chemical equations must always be balanced. Balanced chemical equations have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio. Mass is always conserved in chemical reactions.

Vocabulary

- **Chemical reaction** - The process in which one or more substances are changed into one or more new substances.
- **Reactants** - The starting materials in a reaction.
- **Products** - Materials present at the end of a reaction.
- **Balanced chemical equation** - A chemical equation in which the number of each type of atom is equal on the two sides of the equation.
- **Subscripts** - Part of the chemical formulas of the reactants and products that indicate the number of atoms of the preceding element.
- **Coefficient** - A small whole number that appears in front of a formula in a balanced chemical equation.

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7.5: Acid–Base and Gas Evolution Reactions

Learning Objectives

- Identify when a reaction will evolve a gas.

Neutralization Reactions

Acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen-ion-containing compound and the base is a hydroxide-ion-containing compound, water is also a product. The general reaction is as follows:

$$\textbf{acid} + \textbf{base} \rightarrow \textbf{water} + \textbf{salt}$$

The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:

$$\mathbf{NaOH\,(aq) + HCl\,(aq) \rightarrow NaCl\,(aq) + H_2O\ (\ell)} \tag{7.5.1}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$\mathbf{2\,NaOH\,(aq) + H_2SO_4\,(aq) \rightarrow Na_2SO_4\,(aq) + 2\,H_2O\ (\ell)} \tag{7.5.2}$$

Example 7.5.1: Neutralizing Nitric Acid

Nitric acid (HNO_3(aq)) can be neutralized by calcium hydroxide ($Ca(OH)_2$(aq)). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

Solution

Solutions to Example 7.8.1

Steps	Explanation	Equation
Write the unbalanced equation.	This is a double displacement reaction, so the cations and anions swap to create new products.	$Ca(OH)_2(aq) + HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(\ell)$
Balance the equation.	Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of HNO_3 to provide H^+ ions	$Ca(OH)_2(aq) + \underline{2}HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + \underline{2}H_2O(\ell)$
Additional step: identify the salt.		The salt formed is calcium nitrate.

Exercise 7.5.1

Hydrocyanic acid ($\mathbf{HCN\,(aq)}$) can be neutralized by potassium hydroxide ($\mathbf{KOH\,(aq)}$). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

Answer

\[\ce{KOH (aq) + HCN(aq) → KCN (aq) + H2O(ℓ)} \nonumber \]

Gas Evolving Reactions

A gas evolution reaction is a chemical process that produces a gas, such as oxygen or carbon dioxide. In the following examples, an acid reacts with a carbonate, producing salt, carbon dioxide, and water, respectively. For example, nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide, and water (Table 7.5.1):

$$\mathbf{2\,HNO_3(aq) + Na_2CO_3(aq) \longrightarrow 2\,NaNO_3(aq) + CO_2(g) + H_2O(l)}$$

Sulfuric acid reacts with calcium carbonate to form calcium sulfate, carbon dioxide, and water:

$$\mathbf{H_2SO_4\,(aq) + CaCO_3\,(aq) \longrightarrow CaSO_4\,(aq) + CO_2(g) + H_2O\,(l)}$$

Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide, and water:

$$\mathbf{2\,HCl\,(aq) + CaCO_3\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)}$$

Figure 7.5.1 demonstrates this type of reaction:

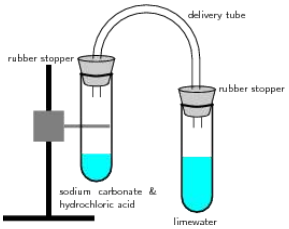


Figure 7.5.1: Reaction of acids with carbonates. In this reaction setup, lime water (water + calcium hydroxide) is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

In this reaction setup, lime water, a dilute calcium hydroxide ($Ca(OH)_2$) solution, is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

Table 7.5.1: Types of Compounds That Undergo Gas-Evolution Reactions

Reactant Type	Intermediate Product	Gas Evolved	Example
sulfide	none	H_2S	$2\,HCl\,(aq) + K_2S \rightarrow H_2S\,(g) + 2\,KCl\,(aq)$
carbonates and bicarbonates	H_2CO_3	CO_2	$2\,HCl\,(aq) + K_2CO_2 \rightarrow H_2O\,(l) + CO_2\,(g)$
sulfites and bisulfites	H_2SO_3	SO_2	$2\,HCl\,(aq) + K_2SO_2 \rightarrow H_2O\,(l) + SO_2\,(g)$
ammonia	NH_4OH	NH_3	\(\ce{NH4Cl(aq) + KOH \rightarrow H2O (l) + NH3(g) + 2KCl (aq)}\)

The gas-evolving experiment lime water is illustrated in the following video:



***Video* 7.5.1:** *Carbon Dioxide (CO_2) & Limewater (Chemical Reaction). As the reaction proceeds, the limewater on the turns from clear to milky; this is due to the $CO_2(g)$ reacting with the aqueous calcium hydroxide to form calcium carbonate, which is only slightly soluble in water.*

When this experiment is repeated with nitric or sulfuric acid instead of HCl, it yields the same results: the clear limewater turns milky, indicating the production of carbon dioxide. Another method to chemically generate gas is the oxidation of metals in acidic solutions. This reaction will yield a metal salt and hydrogen gas.

$$2\,HCl\,(aq) + Zn\,(s) \rightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Here, hydrochloric acid oxidizes zinc to produce an aqueous metal salt and hydrogen gas bubbles. Recall that oxidation refers to a loss of electrons, and reduction refers to the gain of electrons. In the above redox reaction, neutral zinc is oxidized to Zn^{2+}, and the acid, H^+, is reduced to $H_2(g)$. The oxidation of metals by strong acids is another common example of a gas evolution reaction.

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7.6: Oxidation–Reduction Reactions

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

In the course of a chemical reaction between a metal and a nonmetal, electrons are transferred from the metal atoms to the nonmetal atoms. For example, when zinc metal is mixed with sulfur and heated, the compound zinc sulfide is produced. Two valence electrons from each zinc atom are transferred to each sulfur atom.

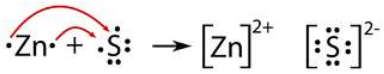


Figure 7.6.1: Reaction between zinc and sulfur.

Since the zinc is losing electrons in the reaction, it is being oxidized. The sulfur is gaining electrons and is thus being reduced. An **oxidation-reduction reaction** is a reaction that involves the full or partial transfer of electrons from one reactant to another. **Oxidation** is the full or partial loss of electrons or the gain of oxygen. **Reduction** is the full or partial gain of electrons or the loss of oxygen. A **redox reaction** is another term for an oxidation-reduction reaction.

Each of these processes can be shown in a separate equation called a half-reaction. A **half-reaction** is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.

$$\underbrace{Zn \longrightarrow Zn_2^{2+} + e^-}_{\text{Oxidation}} \tag{7.6.1}$$

$$\underbrace{S^+ \; 2\,e^- \longrightarrow S^{2-}}_{\text{Reduction}} \tag{7.6.2}$$

It is important to remember that the two half-reactions occur simultaneously. The resulting ions that are formed are then attracted to one another in an ionic bond.

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\,Na^+Cl_2 \longrightarrow 2\,NaCl \tag{7.6.3}$$

The half reactions are as follows:

$$\underbrace{2\,Na \longrightarrow 2\,Na^+ + 2\,e^-}_{\text{Oxidation}} \tag{7.6.4}$$

$$\underbrace{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}_{\text{Reduction}} \tag{7.6.5}$$

We will concern ourselves with the balancing of these equations at another time.

Oxidation Numbers

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.

In H_2, both H atoms have an oxidation number of 0.

2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.

In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1.

3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion (H^-), in which case rule 2 prevails].

In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1.

4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

In SO_2, each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 7.6.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in each substance.

a. Cl_2
b. GeO_2
c. $Ca(NO_3)_2$

Solution

a. Cl_2 is the elemental form of chlorine. Rule 1 states that each atom has an oxidation number of 0.
b. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
c. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation

$$x + 3(-2) = -1$$

where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

$$x + (-6) = -1 \quad x = +5$$

Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 7.6.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in the following:

a. H_3PO_4
b. MgO

Answer a

H: +1; O: −2; P: +5

Answer b

Mg: +2, O: −2

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Thus oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

Example 7.6.2: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

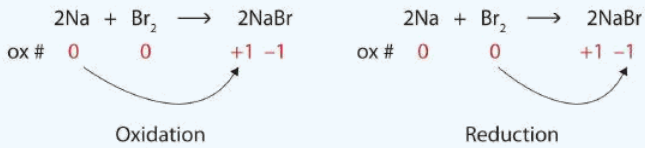
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Equation of sodium and bromine reacting, labeled with sodium's oxidation number change from 0 to +1 and bromine's oxidation number change from 0 to -1

Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 7.6.2: Oxidation of Carbon

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

$$C + O_2 \rightarrow CO_2$$

Answer

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

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\overset{+7}{MnO_4^-}(aq) + 5\overset{-1}{H_2O_2}(l) \rightarrow 2\overset{+2}{Mn^{2+}}(aq) + 5\overset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve $\mathbf{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor.

$$\mathbf{2H_2}\,(g) + \mathbf{O_2}\,(g) \rightarrow \mathbf{2H_2O}\,(g) \tag{7.6.6}$$

Notice that this reaction also qualifies as a combination reaction.

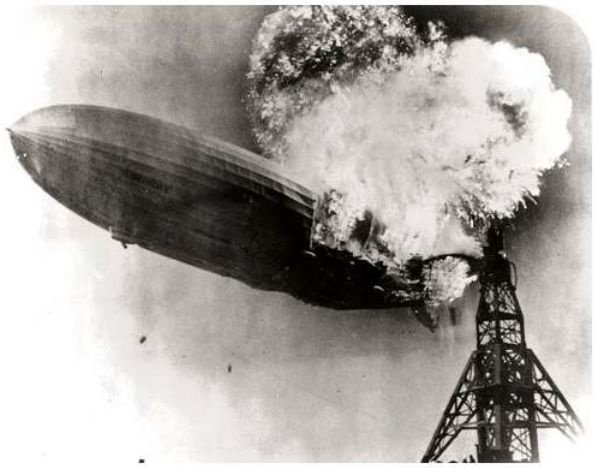


Figure **7.6.2**: Explosion of the Hindenberg.

The *Hindenberg* was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water (Equation **7.6.6**).

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane ($\mathbf{C_3H_8}$) is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathbf{C_3H_8}\,(g) + \mathbf{5O_2}\,(g) \rightarrow \mathbf{3CO_2}\,(g) + \mathbf{4H_2O}\,(g)$$

Example **7.6.3**: Combustion of Ethanol

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is $\mathbf{C_2H_5OH}$. Write the balanced equation for the combustion of ethanol.

Solution

Solutions to Example 7.9.3

Steps	Example Solution
Write the unbalanced reaction.	$\mathbf{C_2H_5OH}\,(l) + \mathbf{O_2}\,(g) \rightarrow \mathbf{CO_2}\,(g) + \mathbf{H_2O}\,(g)$ Ethanol and atmospheric oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.
Balance the equation.	$\mathbf{C_2H_5OH}\,(l) + \mathbf{3O_2}\,(g) \rightarrow \mathbf{2CO_2}\,(g) + \mathbf{3H_2O}\,(g)$
Think about your result.	Combustion reactions must have oxygen as a reactant. Note that the water produced is in the gas state, rather than the liquid state, because of the high temperatures that accompany a combustion reaction.

? Exercise 7.6.3: Combustion of Hexane

Write the balanced equation for the combustion of hexane, C_6H_{14}

Answer

$$2\,C_6H_{14}\,(\ell) + 19\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 14\,H_2O(\ell)$$

Contributors & Affiliations

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7.7: Classifying Chemical Reactions

Learning Objectives

- Classify a chemical reaction as a synthesis, decomposition, single replacement, double replacement, or a combustion reaction.
- Predict the products of simple reactions.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types: acid–base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation–reduction reactions. The general forms of these five kinds of reactions are summarized in Table **7.7.1**, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

Table **7.7.1:** *Basic Types of Chemical Reactions*

Name of Reaction	General Form	Examples
Oxidation–Reduction (redox)	oxidant + reductant → reduced oxidant + oxidized reductant	$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$
Acid–Base	acid + base → salt	$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
Exchange: Single Replacement	AB + C → AC + B	$ZnCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Zn(s)$
Exchange: Double Replacement	AB + CD → AD + CB	$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
Combination (Synthesis)	A + B → AB	$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
Decomposition	AB → A + B	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions are one kind of exchange reaction—the formation of an insoluble salt, such as barium sulfate, when solutions of two soluble salts are mixed together.

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$\mathbf{A + B \rightarrow AB}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$\mathbf{2Na\,(\mathit{s}) + Cl_2\,(\mathit{g}) \rightarrow 2NaCl\,(\mathit{s})}$$

Notice that in order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules ($\mathbf{H_2}$, $\mathbf{N_2}$, $\mathbf{O_2}$, $\mathbf{F_2}$, $\mathbf{Cl_2}$, $\mathbf{Br_2}$, and $\mathbf{I_2}$).

One type of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide:

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

Sulfur reacts with oxygen to form sulfur dioxide:

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g)$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to form sulfur trioxide:

$$2S\,(s) + 3O_2\,(g) \rightarrow 2SO_3\,(g)$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

$$2Fe\,(s) + O_2\,(g) \rightarrow 2FeO\,(s)$$

$$4Fe\,(s) + 3O_2\,(g) \rightarrow 2Fe_2O_3\,(s)$$

Example 7.7.1: Combustion of Solid Potassium

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

Solution

Solutions to Example 7.10.1

Steps	Example Solution
Plan the problem.	Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes K^+, while the oxide ion is O^{2-}.
Solve.	The skeleton (unbalanced) equation: $$K\,(s) + O_2\,(g) \rightarrow K_2O\,(s)$$ The equation is then easily balanced with coefficients. $$4K\,(s) + O_2\,(g) \rightarrow 2K_2O\,(s)$$
Think about your result.	Formulas are correct and the resulting combination reaction is balanced.

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$$

Two compounds may also react to form a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide:

$$CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(aq)$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)$$



Figure **7.7.1**: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

? Exercise 7.7.1

a. Write the chemical equation for the synthesis of silver bromide, **AgBr**.
b. Predict the products for the following reaction: $CO_2\,(g) + H_2O\,(l)$

Answer a:

$$2Ag + Br_2 \rightarrow 2AgBr$$

Answer b:

$$CO_2\,(g) + H_2O\,(l) \rightarrow H_2CO_3$$

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$AB \rightarrow A + B$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas:

$$2HgO\,(s) \rightarrow 2Hg\,(l) + O_2\,(g)$$



***Video* 7.7.2:** *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.*

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water:

$$2NaOH\,(s) \rightarrow Na_2O\,(s) + H_2O\,(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water:

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$$

Example 7.7.2: Electrolysis of Water

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Solution

Solutions to Example 7.10.2

Steps	Example Solution
Plan the problem.	Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules.
Solve.	The skeleton (unbalanced) equation: $$H_2O\,(l) \xrightarrow{elec} H_2\,(g) + O_2\,(g)$$ Note the abbreviation "**elec**" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation. $$2H_2O\,(l) \xrightarrow{elec} 2H_2\,(g) + O_2\,(g)$$
Think about your result.	The products are elements and the equation is balanced.

Exercise 7.7.2

Write the chemical equation for the decomposition of:

a. Al_2O_3
b. Ag_2S

Answer a

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

Answer b

$$Ag_2S \rightarrow 2Ag + S$$

Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element **A** is a metal and replaces element **B**, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$\mathbf{Y + XZ \rightarrow XY + Z}$$

where **Y** is a nonmetal and replaces the nonmetal **Z** in the compound with **X**.

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\mathbf{Mg\,(\mathit{s}) + Cu(NO_3)_2\,(\mathit{aq}) \rightarrow Mg(NO_3)_2\,(\mathit{aq}) + Cu\,(\mathit{s})}$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$\mathbf{Zn\,(\mathit{s}) + 2HCl\,(\mathit{aq}) \rightarrow ZnCl_2\,(\mathit{aq}) + H_2\,(\mathit{g})}$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All Group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$\mathbf{2Na\,(\mathit{s}) + 2H_2O\,(\mathit{l}) \rightarrow 2NaOH\,(\mathit{aq}) + H_2\,(\mathit{g})}$$



Figure **7.7.2**: (First image) Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Second image) Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\mathbf{Cl_2\,(\mathit{g}) + 2NaBr\,(\mathit{aq}) \rightarrow 2NaCl\,(\mathit{aq}) + Br_2\,(\mathit{l})}$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

Example 7.7.3

What are the products of the reaction between solid aluminum (**Al**) and iron (III) oxide ($\mathbf{Fe_2O_3}$)?

Solution

Solutions to Example 7.10.3

Steps	Example Solution
Plan the problem.	To predict the products, we need to know that aluminum will replace iron and form aluminum oxide (the metal will replace the metal ion in the compound). Aluminum has a charge of $+3$ and oxygen has a charge of -2. The compound formed between aluminum and oxygen, therefore, will be Al_2O_3. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products.
Solve.	The unbalanced equation will be: $$Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$$ and the balanced equation will be: $$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$
Think about your result.	This is a single replacement reaction, and when balanced the coefficients accurately reflect that the iron and aluminum have the same charge in this reaction.

? Exercise 7.7.3

a. Write the chemical equation for the single replacement reaction between zinc solid and lead (II) nitrate solution to produce zinc nitrate solution and solid lead. (Note that zinc forms ions with a $+2$ charge.)

b. Predict the products for the following reaction: $Fe + CuSO_4$. (In this reaction, assume iron forms ions with a $+2$ charge.)

Answer a

$$Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2$$

Answer b

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

Double Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$AB + CD \rightarrow AD + BC$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow 2KNO_3\,(aq) + PbI_2\,(s) \qquad (7.7.1)$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (Figure **7.7.3**). The other product of the reaction, potassium nitrate, remains soluble.



Figure **7.7.3**: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation 7.7.1). (CC BY-SA 3.0; PRHaney).

Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas:

$$\mathrm{Na_2S}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{H_2S}\,(g)$$

Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

Example 7.7.4

Write a complete and balanced chemical equation for the double-replacement reaction $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed).

Solution

Solutions to Example 7.10.4

Steps	Example Solution
Plan the problem.	The production of a gas drives the reaction.
Solve.	The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is: $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$
Think about your result.	This is a double replacement reaction. All formulas are correct and the equation is balanced.

Exercise 7.7.4

Write a complete and balanced chemical equation for the double-replacement reaction $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms).

Answer a:

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water:

$$\mathrm{Na_2CO_3}\,(aq) + \mathrm{2HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

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CHAPTER OVERVIEW

8: Rates of Reactions

8.1: Introduction to Rates of Reactions
8.2: Factors that Impact Reaction Rates

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8.1: Introduction to Rates of Reactions

Learning Outcomes

- Define reaction rate.
- Define catalyst and explain its behavior in a chemical reaction.
- Describe how temperatures, concentration or pressure of reactant, and a catalyst affect the reaction rate.
- Explain the concept of activation energy.
- Label a diagram with reactants, products, enthalpy of forward and reverse reactions, activation energy of forward and reverse reactions, and activated complex.
- Calculate the enthalpy and activation energy with data on a reaction diagram.

Chemical kinetics is the study of the rates of chemical reactions. In this lesson, you will learn how to express the rate of a chemical reaction and about various factors that influence reaction rates.

Expressing Reaction Rate

Chemical reactions vary widely in the speeds with which they occur. Some reactions occur very quickly. It a lighted match is brought into contact with lighter fluid or another flammable liquid, it erupts into flame instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes 11.0 seconds (s) to run a 100 meter (\left(m \right)\) dash, his rate or speed is given by the distance traveled divided by the time (see figure below).

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s} \tag{8.1.1}$$

The sprinter's average running rate for the race is $9.09\ \text{m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must the be greater than $9.09\ \text{m/s}$ so that taken over the entire race, the average ends up at $9.09\ \text{m/s}$.

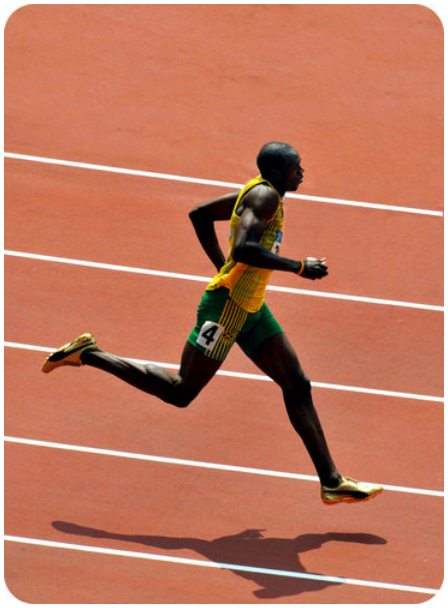


Figure 8.1.1: Usain Bolt set the world record for the 100 meter dash in 2009 with a time of 9.58 seconds. His average running rate over the course of this race was $10.4\ \text{m/s}$, or $23.4\ \text{mph}$.

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** *is the change in concentration of a reactant or product with time*. Suppose that a simple reaction were to take place in which a 1.00 molar

(M) aqueous solution of substance A was converted to substance B.

$$\mathrm{A}\,(aq) \rightarrow \mathrm{B}\,(aq) \tag{8.1.2}$$

Suppose that after 20.0 seconds, the concentration of A had dropped from 1.00 M to 0.72 M as it was being converted to substance B. We can express the rate of this reaction as the change in concentration of A divided by the time.

$$\text{rate} = -\frac{\Delta\,[\mathrm{A}]}{\Delta t} = -\frac{[\mathrm{A}]_{\text{final}} - [\mathrm{A}]_{\text{initial}}}{\Delta t} \tag{8.1.3}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of A is its final concentration minus its initial concentration. Because the concentration of A is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive, and the units are molarity per second or M/s.

$$\text{rate} = -\frac{0.72\ \mathrm{M} - 1.00\ \mathrm{M}}{20.0\ \mathrm{s}} = -\frac{-0.28\ \mathrm{M}}{20.0\ \mathrm{s}} = 0.041\ \mathrm{M/s} \tag{8.1.4}$$

Over the first 20.0 seconds of this reaction, the molarity of A decreases by an average rate of 0.041 M every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second (M/s).

Collision Theory

The behavior of the reactant atoms, molecules, or ions is responsible for the rates of a given chemical reaction. **Collision theory** *is a set of principles based around the idea that reactant particles form products when they collide with one another, but only when those collisions have enough kinetic energy and the correct orientation to cause a reaction.* Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other produce. The first collision is called an ineffective collision, while the second collision is called an effective collision.

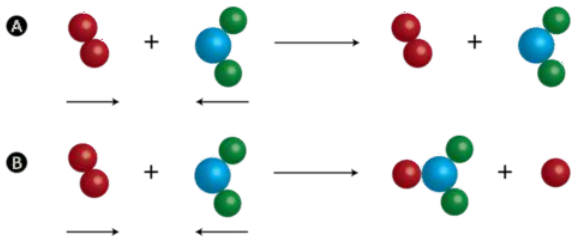


Figure 8.1.2: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break and a chemical reaction more likely to occur when those particles collide with other particles. Additionally, more energetic particles have more forceful collisions, which also increases the likelihood that a rearrangement of atoms will take place. The **activation energy** *for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction*. Some reactions occur readily at room temperature because most of the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy to react unless more is provided by an external source of heat.

Potential Energy Diagrams

Then energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, sometimes called a reaction progress curve. A **potential energy diagram** *shows the change in the potential energy of a system as reactants are converted into products*. The figure below shows basic potential energy diagrams for an endothermic (left) and an exothermic (right) reaction. Recall that the enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the

endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

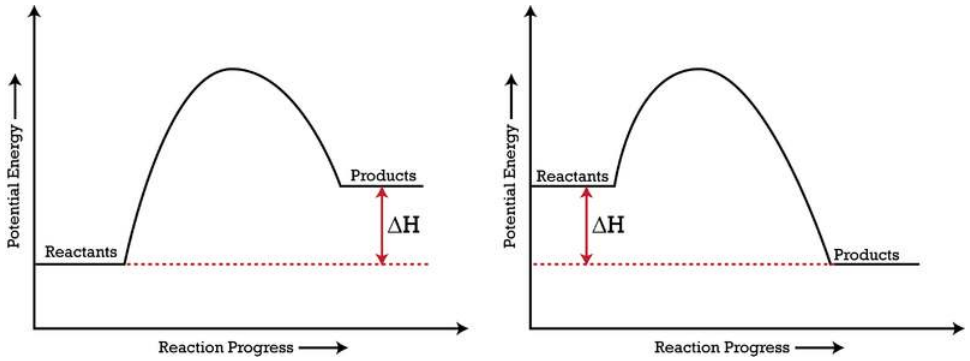


Figure 8.1.3: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and ΔH is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and ΔH is negative.

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome this barrier (see figure below).

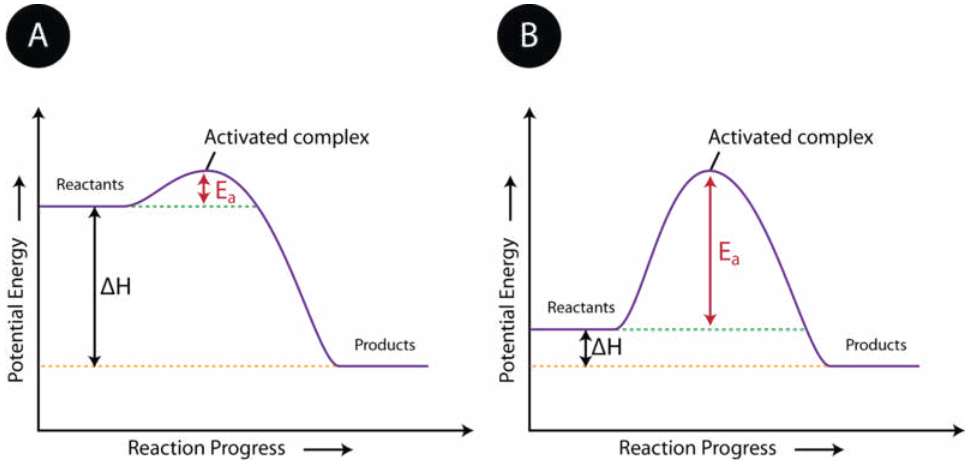


Figure 8.1.4: The activation energy (E_a) of a reaction is the barrier that must be overcome in order for the reactants to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

As discussed earlier, reactant particles sometimes collide with one another and yet remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** *is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier*. Because of its high energy, the activated complex exists only for an extremely short period of time (about 10^{-13} s). The activated complex is equally likely to either reform the original reactants or go on to form the products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of most activated complexes.

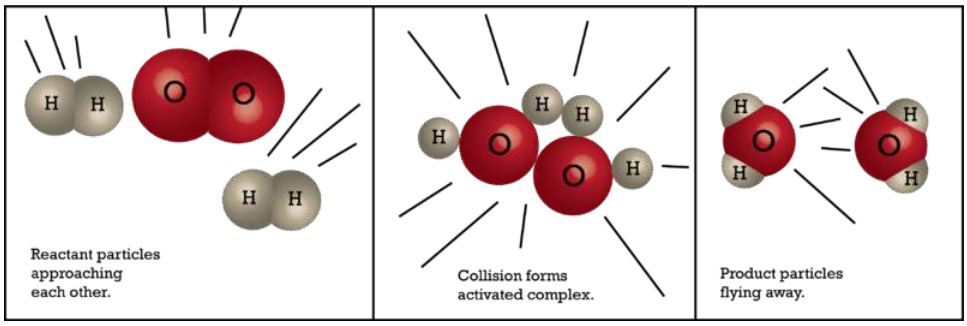


Figure 8.1.5: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

Factors Affecting Reaction Rates

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reaction conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

Concentration

Increasing the concentration of one or more of the reacting substances generally increases the reaction rate. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the frequency of collisions between the reactants, the rate increases as the concentration increases.

Pressure

When the pressure of a gas is increased, its particles are forced closer together, decreasing the amount of empty space between them. Therefore, an increase in the pressure of a gas is also an increase in the concentration of the gas. For gaseous reactions, an increase in pressure increases the rate of reaction for the same reasons as described above for an increase in concentration. Higher gas pressure leads to a greater frequency of collisions between reacting particles.

Surface Area

A large log placed in a fire will burn relatively slowly. If the same mass of wood were added to the fire in the form of small twigs, they would burn much more quickly. This is because the twigs provide a greater surface are than the log does. An increase in the surface area of a reactant increases the rate of a reaction. Surface area is larger when a given amount of a solid is present as smaller particles. A powdered reactant has a greater surface area than the same reactant as a solid chunk. In order to increase the surface area of a substance, it may be ground into smaller particles or dissolved into a liquid. In solution, the dissolved particles are separated from each other and will react more quickly with other reactants. The figure below shows the unfortunate result of high surface area in an unwanted combustion reaction. Small particles of grain dust are very susceptible to rapid reactions with oxygen, which can result in violent explosions and quick-burning fires.



Figure 8.1.6: This grain elevator in Kansas exploded in 1998. The tiny size of the reacting particles (grain dust) caused the reaction with oxygen in the air to be violently explosive.

Temperature

Raising the temperature of a chemical reaction results in a higher reaction rate. When the reactant particles are heated, they move faster and faster, resulting in a greater frequency of collisions. An even more important effect of the temperature increase is that the collisions occur with a greater force, which means the reactants are more likely to surmount the activation energy barrier and go on

to form products. Increasing the temperature of a reaction increases not only the frequency of collisions, but also the percentage of those collisions that are effective, resulting in an increased reaction rate.

Paper is certainly a highly combustible material, but paper does not burn at room temperature because the activation energy for the reaction is too high. The vast majority of collisions between oxygen molecules and the paper are ineffective. However, when the paper is heated by the flame from a match, it reaches a point where the molecules now have enough energy to react. The reaction is very exothermic, so the heat released by the initial reaction will provide enough energy to allow the reaction to continue, even if the match is removed. The paper continues to burn rapidly until it is gone.

Catalysts

The rates of some chemical reactions can be increased dramatically by introducing certain other substances into the reaction mixture. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and it can be found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** *is a substance that increases the rate of a chemical reaction without being used up in the reaction*. It accomplishes this task by providing an alternate reaction pathway that has a lower activation energy barrier. After the reaction occurs, a catalyst returns to its original state, so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$2H_2O_2\,(aq) \overset{MnO_2}{\rightarrow} 2H_2O\,(l) + O_2\,(g) \tag{8.1.5}$$

A catalyst works by changing the mechanism of the reaction, which can be though of as the specific set of smaller steps by which the reactants become products. The important point is that the use of a catalyst lowers the overall activation energy of the reaction (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

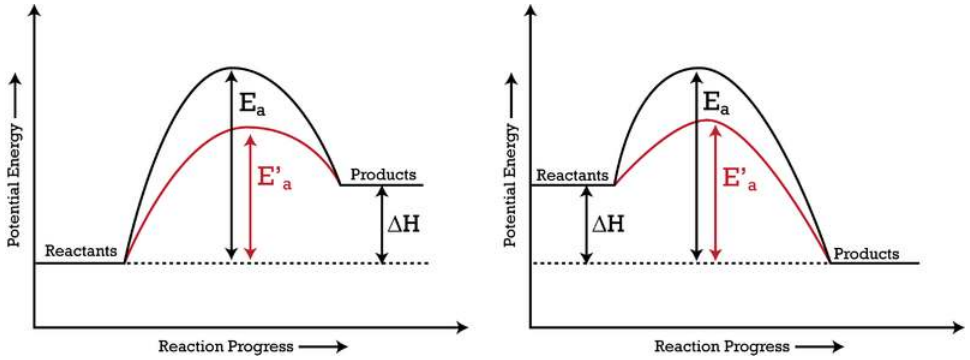


Figure **8.1.7**: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E'_a. The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

Catalysts are extremely important parts of many chemical reactions. Enzymes in your body act as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

Contributors and Attributions

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8.2: Factors that Impact Reaction Rates

Learning Objectives

- Describe the conditions for successful collisions that cause reactions.
- Describe *rate* in terms of the conditions of successful collisions.
- Describe how changing the temperature, concentration of a reactant, or surface area of a reaction affects the rate of a reaction.
- Define a catalyst and how a catalyst affects the rate of a reaction.

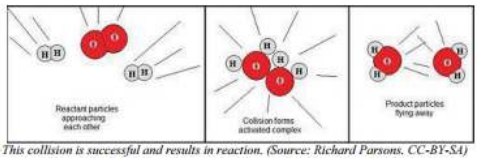
We know that a chemical system can be made up of atoms (H_2, N_2, K, etc.), ions (NO_3^-, Cl^-, Na^+, etc.), or molecules (H_2O, $C_{12}H_{22}O_{11}$, etc.). We also know that in a chemical system, these particles are moving around in random motion. The **collision theory** explains why reactions occur at this particle level between these atoms, ions, and/or molecules. It also explains how it is possible to speed up or slow down reactions that are occurring.

Collision Theory

The collision theory provides us with the ability to predict what conditions are necessary for a successful reaction to take place. These conditions include:

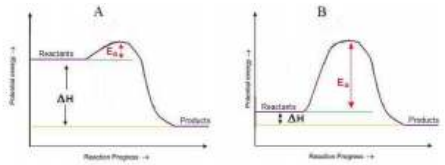
1. The particles must collide with each other.
2. The particles must collide with sufficient energy to break the old bonds.
3. The particles must have proper orientation.

A chemical reaction involves breaking bonds in the reactants, rearranging the atoms into new groupings (the products), and forming new bonds in the products.



This collision is successful and results in reaction. (Source: Richard Parsons. CC-BY-SA)

Therefore, a collision must not only occur between reactant particles, but the collision also has to have sufficient energy to break all the reactant bonds that need to be broken in order to form the products. Some reactions need less collision energy than others. The amount of energy that reactant particles must have in order to break the old bonds for a reaction to occur is called the **activation energy**, abbreviated E_a. Another way to think of this is to look at an energy diagram, as shown in the figure. Particles must be able to get over the "bump"—the activation energy—if they are going to react. If the reactant particles collide with less than the activation energy, the particles will rebound (bounce off of each other), and no reaction will occur.



Each reaction has its own activation energy, E_a. The smaller the "bump", the less energy particles must have to react.

Reaction Rate

Chemists use reactions to generate a product for which they have a use. For the most part, the reactions that produce some desired compound are only useful if the reaction occurs at a reasonable rate. For example, using a reaction to produce brake fluid would not be useful if the reaction required 8,000 years to complete the product. Such a reaction would also not be useful if the reaction was so fast that it was explosive. For these reasons, chemists wish to be able to control reaction rates. In some cases, chemists wish to speed up reactions that are too slow or slow down reactions that are too fast. In order to gain any control over reaction rates, we must know the factors that affect reaction rates. Chemists have identified many factors that affect the rate of a reaction.

The rate, or speed, at which a reaction occurs depends on the frequency of successful collisions. Remember, a successful collision occurs when two reactants collide with enough energy and with the right orientation. That means if there is an increase in the number of

collisions, an increase in the number of particles that have enough energy to react, and/or an increase in the number of particles with the correct orientation, the rate of reaction will increase.

Effect of Temperature on Rate of Reaction

The rate of reaction was discussed in terms of three factors: collision frequency, the collision energy, and the geometric orientation. Remember that the collision frequency is the number of collisions per second. The collision frequency is dependent, among other factors, on the temperature of the reaction.

When the temperature is increased, the average velocity of the particles is increased. The average kinetic energy of these particles is also increased. The result is that the particles will collide more frequently, because the particles move around faster and will encounter more reactant particles. However, this is only a minor part of the reason why the rate is increased. Just because the particles are colliding more frequently does not mean that the reaction will definitely occur.

The major effect of increasing the temperature is that more of the particles that collide will have the amount of energy needed to have an effective collision. In other words, more particles will have the necessary activation energy.

At room temperature, the hydrogen and oxygen in the atmosphere do not have sufficient energy to attain the activation energy needed to produce water:

$$\mathrm{O_2}\,(g) + \mathrm{H_2}\,(g) \rightarrow \text{No reaction}$$

At any one moment in the atmosphere, there are many collisions occurring between these two reactants. But what we find is that water is not formed from the oxygen and hydrogen molecules colliding in the atmosphere, because the activation energy barrier is just too high, and all the collisions are resulting in rebound. When we increase the temperature of the reactants or give them energy in some other way, the molecules have the necessary activation energy and are able to react to produce water:

$$\mathrm{O_2}\,(g) + \mathrm{H_2}\,(g) \rightarrow \mathrm{H_2O}\,(l)$$

There are times when the rate of a reaction needs to be slowed down. Lowering the temperature could also be used to decrease the number of collisions that would occur and lowering the temperature would also reduce the kinetic energy available for activation energy. If the particles have insufficient activation energy, the collisions will result in rebound rather than reaction. Using this idea, when the rate of a reaction needs to be lower, keeping the particles from having sufficient activation energy will definitely keep the reaction at a lower rate.

Society uses the effects of temperature on reaction rate every day. Food storage is a prime example of how the temperature effect on reaction rate is utilized by society. Consumers store food in freezers and refrigerators to slow down the processes that cause it to spoil. The decrease in temperature decreases the rate at which food will break down or be broken down by bacteria. In the early years of the 20th century, explorers were fascinated with being the first to reach the South Pole. In order to attempt such a difficult task at a time without most of the technology that we take for granted today, they devised a variety of ways of surviving. One method was to store their food in the snow to be used later during their advances to the pole. On some explorations, they buried so much food that they didn't need to use all of it, and some was left behind. Many years later, when this food was located and thawed, it was found to still be edible.

When milk, for example, is stored in the refrigerator, the molecules in the milk have less energy. This means that while molecules will still collide with other molecules, few of them will react (which means in this case "spoil") because the molecules do not have sufficient energy to overcome the activation energy barrier. The molecules do have energy and are colliding, however, and so, over time, even in the refrigerator, the milk will spoil. Eventually the higher energy molecules will gain the energy needed to react and when enough of these reactions occur, the milk becomes "soured".

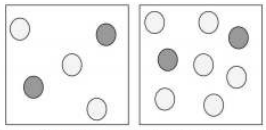
However, if that same carton of milk was at room temperature, the milk would react (in other words, "spoil") much more quickly. Most of the molecules would have sufficient energy to overcome the energy barrier at room temperature, and many more collisions would occur. This allows for the milk to spoil in a fairly short amount of time. This is also the reason why most fruits and vegetables ripen in the summer when the temperature is much warmer. You may have experienced this first hand if you have ever bitten into an unripe banana—it was probably sour tasting and might even have felt like biting into a piece of wood! When a banana ripens, numerous reactions occur that produce all the compounds that we expect to taste in a banana. But this can only happen if the temperature is high enough to allow these reactions to make those products.

Effect of Concentration on Rate of Reaction

If you had an enclosed space, like a classroom, and there was one red ball and one green ball flying around the room in random motion, undergoing perfectly elastic collisions with the walls and with each other, in a given amount of time, the balls would collide with each other a certain number of times determined by probability. If you now put two red balls and one green ball in the room under the same

conditions, the probability of a collision between a red ball and the green ball would exactly double. The green ball would have twice the chance of encountering a red ball in the same amount of time.

In terms of chemical reactions, a similar situation exists. Particles of two gaseous reactants or two reactants in solution have a certain probability of undergoing collisions with each other in a reaction vessel. If you double the concentration of either reactant, the probability of a collision doubles. The rate of reaction is proportional to the number of collisions per unit time. If one concentration is doubled, the number of collisions will also double. Assuming that the percent of collisions that are successful does not change, then having twice as many collisions will result in twice as many successful collisions. The rate of reaction is proportional to the number of collisions over time; increasing the concentration of either reactant increases the number of collisions, and therefore increases the number of successful collisions and the reaction rate.



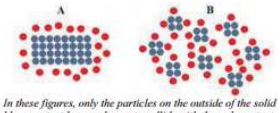
The reaction mixture on the left is less concentrated, so particles will not collide as often. The reaction will be slower. Because the reacting particles on the right image have a greater change of colliding, the reaction will go faster. CC – Tracy Poulsen

For example, the chemical test used to identify a gas as oxygen, or not, relies on the fact that increasing the concentration of a reactant increases reaction rate. The reaction we call combustion refers to a reaction in which a flammable substance reacts with oxygen. If we light a wooden splint (a thin splinter of wood) on fire and then blow the fire out, the splint will continue to glow in air for a period of time. If we insert that glowing splint into any gas that does not contain oxygen, the splint will immediately cease to glow—that is, the reaction stops. Oxygen is the only gas that will support combustion, Air is approximately 20% oxygen gas. If we take that glowing splint and insert it into pure oxygen gas, the reaction will increase its rate by a factor of five, since pure oxygen has 5 times the concentration of oxygen that is in the air. When the reaction occurring on the glowing splint increases its rate by a factor of five, the glowing splint will suddenly burst back into full flame. This test, of thrusting a glowing splint into a gas, is used to identify the gas as oxygen. Only a greater concentration of oxygen than that found in air will cause the glowing splint to burst into flame.

Effect of Surface Area on Rate of Reaction

The very first requirement for a reaction to occur between reactant particles is that the particles must collide with one another. The previous section pointed out how increasing the concentration of the reactants increases reaction rate because it increases the frequency of collisions between particles. It can be shown that the number of collisions that occur between reactant particles is also dependent on the surface area of solid reactants. Consider a reaction between reactant RED and reactant BLUE in which reactant blue is in the form of a single lump. Then compare this to the same reaction where reactant blue has been broken up into many smaller pieces.

In the diagram, only the blue particles on the outside surface of the lump are available for collision with reactant red. The blue particles on the interior of the lump are protected by the blue particles on the surface. In Figure A, if you count the number of blue particles available for collision, you will find that only 20 blue particles could be struck by a particle of reactant red. In Figure A, there are a number of blue particles on the interior of the lump that cannot be struck. In Figure B, however, the lump has been broken up into smaller pieces and all the interior blue particles are now on a surface and available for collision. In Figure B, more collisions between the blue and red will occur, and therefore, the reaction in Figure B will occur at a faster rate than the same reaction in Figure A. Increasing the surface area of a reactant increases the frequency of collisions and increases the reaction rate.



In these figures, only the particles on the outside of the solid blue reactant have a chance to collide with the red reactant. In figure B, the same amount of solid reactant as used in A was crushed into smaller particles. This means that more particles on the outside of the reactant have an opportunity to collide with the red reactant and speeds up the reaction.

Several smaller particles have more surface area than one large particle. The more surface area that is available for particles to collide, the faster the reaction will occur. You can see an example of this in everyday life if you have ever tried to start a fire in the fireplace. If you hold a match up against a large log in an attempt to start the log burning, you will find it to be an unsuccessful effort. Holding a match against a large log will not cause enough reactions to occur in order to keep the fire going by providing sufficient activation energy for further reactions. In order to start a wood fire, it is common to break a log up into many small, thin sticks called kindling. These thinner sticks of wood provide many times the surface area of a single log. The match will successfully cause enough reactions in the kindling so that sufficient heat is given off to provide activation energy for further reactions.

There have been, unfortunately, cases where serious accidents were caused by the failure to understand the relationship between surface area and reaction rate. One such example occurred in flour mills. A grain of wheat is not very flammable. It takes significant effort to get a grain of wheat to burn. If the grain of wheat, however, is pulverized and scattered through the air, only a spark is necessary to cause an explosion. When the wheat is ground to make flour, it is pulverized into a fine powder and some of the powder gets scattered around in the air. A small spark then, is sufficient to start a very rapid reaction which can destroy the entire flour mill. In a 10-year period from 1988 to 1998, there were 129 grain dust explosions in mills in the United States. Efforts are now made in flour mills to have huge fans circulate the air in the mill through filters to remove the majority of the flour dust particles.

Another example is in the operation of coal mines. Coal will of course burn, but it takes an effort to get the coal started; once it is burning, it burns slowly because only the surface particles are available to collide with oxygen particles. The interior particles of coal have to wait

until the outer surface of the coal lump burns off before they can collide with oxygen. In coal mines, huge blocks of coal must be broken up before the coal can be brought out of the mine. In the process of breaking up the huge blocks of coal, drills are used to drill into the walls of coal. This drilling produces fine coal dust that mixes into the air; then a spark from a tool can cause a massive explosion in the mine. There are explosions in coal mines for other reasons, but coal dust explosions have contributed to the death of many miners. In modern coal mines, lawn sprinklers are used to spray water through the air in the mine and this reduces the coal dust in the air, and eliminates coal dust explosions.

Effect of a Catalyst on Rate of Reaction

The final factor that affects the rate of the reaction is the effect of a catalyst. A **catalyst** is a substance that speeds up the rate of the reaction, without being consumed by the reaction itself.

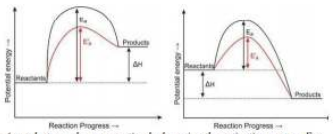
In the reaction of potassium chlorate breaking down to potassium chloride and oxygen, a catalyst is available to make this reaction occur much faster than it would occur by itself under room conditions. The reaction is:

$$2KClO_3\,(s) \xrightarrow{MnO_2(s)} 2KCl\,(s) + 3O_2\,(g)$$

The catalyst is manganese dioxide and its presence causes the reaction shown above to run many times faster than it occurs without the catalyst. When the reaction has reached completion, the MnO_2 can be removed from the reaction vessel and its condition is exactly the same as it was before the reaction. This is part of the definition of a catalyst—that it is not consumed by the reaction. You should note that the catalyst is not written into the equation as a reactant or a product, but is noted above the yields arrow. This is standard notation for the use of a catalyst.

Some reactions occur very slowly without the presence of a catalyst. In other words, the activation energy for these reactions is very high. When the catalyst is added, the activation energy is lowered because the catalyst provides a new reaction pathway with lower activation energy.

In the figure on the right, the endothermic reaction shows the catalyst reaction in red with the lower activation energy, designated E_a'. The new reaction pathway has lower activation energy but has no effect on the energy of the reactants, the products, or the value of ΔH. The same is true for the exothermic reaction. The activation energy of the catalyzed reaction is lower than that of the uncatalyzed reaction. The new reaction pathway provided by the catalyst affects the energy required for reactant bonds to break, and product bonds to form.



A catalyst speeds up a reaction by lowering the activation energy, E_a.. Because less energy is required to react, more particles have the necessary energy.

While many reactions in the laboratory can be increased by increasing the temperature, this is not possible for all of the reactions that occur in our bodies throughout our entire lives. In fact, the body needs to be maintained at a very specific temperature: **98.6°F** or **37°C**. Of course there are times, such as when the body is fighting infection, when the body temperature may be increased. But generally, in a healthy person, the temperature is quite consistent. However, many of the reactions that a healthy body depends on could never occur at body temperature. The answer to this dilemma is catalysts—also referred to as enzymes. Many of these enzymes are made in human cells because human DNA carries the directions to make them. However, there are some enzymes required by the body that are not made by human cells. These catalysts must be supplied to our bodies in the food we eat and are called vitamins.

Reversible Reactions

Typically when we think of a chemical reaction, we think of the reactants getting totally used up so that none are left, and that we end up with only products. Also, we generally consider chemical reactions as one-way events. You may well have learned during earlier science classes that this is one way to distinguish chemical change from physical change—physical changes (such as the melting and freezing of ice) are easily reversed, but chemical changes cannot be reversed (pretty tough to un-fry an egg).

Throughout this chaper, we will see that this isn't always the case. We will see that many chemical reactions are, in fact, reversible under the right conditions. And because many reactions can be reversed, our idea of a reaction ending with no reactants left, only products, will need to be modified.

Here are some examples of reactions that can be reversed:

1.

Nitrogen dioxide, NO_2, a reddish-brown gas, reacts to form colorless dinitrogen tetroxide, N_2O_4 :

$$2NO_2(g) \rightarrow N_2O_4(g)$$

But the reaction can also go the other way—dinitrogen tetroxide also readily breaks down to form nitrogen dioxide:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

We typically write a reaction that can go in both directions by using a double arrow (which will sometimes appear as ↔ in these online notes):

$$2NO_2(g) \leftrightarrow N_2O_4(g)$$

Because the reaction continues in both directions at the same time, we never run out of either NO_2 or N_2O_4 . NO_2 is continually being used up to form N_2O_4, but at the same time N_2O_4 is forming more NO_2

2.

When hydrogen gas is passed over heated iron oxide, iron and steam are produced:

(1)	$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H$

The reverse reaction can occur when steam is passed over red-hot iron:

(2)	$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4$

We can write these two equations together as:

(3)	\(\ce{Fe_3O_4(s) + 4H_2(g) \leftrightarrow 3Fe(s) + 4H_2O(g)}\)

When we have a reversible reaction written in this way, we need to be able to distinguish between which way the reaction is headed. As written above in Reaction (3), we would say that in the ***forward reaction***, iron oxide and hydrogen gas, the reactants, produce the products iron and steam.

During the ***reverse reaction***, iron reacts with steam to produce the products iron oxide and hydrogen gas.

It is important to understand the terminology, and to use the terms correctly.

Does it matter which way we write our reversible reaction? It can also be written as

$$3Fe(s) + 4H_2O(g) \leftrightarrow Fe_3O_4(s) + 4H_2(g)$$

Now iron and steam are reactants of the forward direction, and iron oxide and hydrogen gas would be the reactants of the reverse direction.

Summary

- The collision theory explains why reactions occur between atoms, ions, and molecules.
- In order for a reaction to be effective, particles must collide with enough energy, and have the correct orientation.
- With an increase in temperature, there is an increase in energy that can be converted into activation energy in a collision, and that will increase the reaction rate. A decrease in temperature would have the opposite effect.
- With an increase in temperature, there is an increase in the number of collisions.
- Increasing the concentration of a reactant increases the frequency of collisions between reactants and will, therefore, increase the reaction rate.

- Increasing the surface area of a reactant (by breaking a solid reactant into smaller particles) increases the number of particles available for collision and will increase the number of collisions between reactants per unit time.
- A catalyst is a substance that speeds up the rate of the reaction without being consumed by the reaction itself. When a catalyst is added, the activation energy is lowered because the catalyst provides a new reaction pathway with lower activation energy.

Vocabulary

- **Catalyst -** A substance that speeds up the rate of the reaction without being consumed by the reaction itself.
- **Surface area to volume ratio -** The comparison of the volume inside a solid to the area exposed on the surface.

Further Reading/Supplemental Links

- Activation Energy: http://www.mhhe.com/physsci/chemistr...sh/activa2.swf
- learner.org/resources/series61.html The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos, but there is no charge. The website has one video that relates to this lesson called ***Molecules in Action***.
- www.vitamins-guide.net
- en.Wikipedia.org/wiki
- Observing molecules during chemical reactions helps explain the role of catalysts. Dynamic equilibrium is also demonstrated. Molecules in Action (www.learner.org/vod/vod_window.html?pid=806)
- Surface science examines how surfaces react with each other at the molecular level. On the Surface (www.learner.org/vod/vod_window.html?pid=812)

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CHAPTER OVERVIEW

9: Chemical Equilibrium

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In previous science classes, you may have learned that one way to distinguish chemical changes from physical changes is that physical changes—such as the melting and freezing of water—are reversible, but that chemical changes are not. In this chapter, we will see that this simple answer is not necessarily what it seems.

9.1: Chemical Equilibrium

9.2: Le Châtelier's Principle

9.3: The Effect of a Volume Change on Equilibrium

9.4: The Path of a Reaction and the Effect of a Catalyst

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9.1: Chemical Equilibrium

Learning Outcomes

- Explain chemical equilibrium.
- Write expression for calculating K.
- Calculate and compare Q and K values.
- Predict relative amounts of reactants and products based on equilibrium constant K.

Hydrogen and iodine gases react to form hydrogen iodide according to the following reaction:

$$\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$$

$$\text{Forward reaction: } \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightarrow 2\mathrm{HI}\,(g) \tag{9.1.1}$$
$$\text{Reverse reaction: } 2\mathrm{HI}\,(g) \rightarrow \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \tag{9.1.2}$$

Initially, only the forward reaction occurs because no HI is present. As soon as some HI has formed, it begins to decompose back into $\mathrm{H_2}$ and $\mathrm{I_2}$. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of $\mathrm{H_2}$ and $\mathrm{I_2}$ to produce HI becomes equal to the rate of decomposition of HI into $\mathrm{H_2}$ and $\mathrm{I_2}$. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

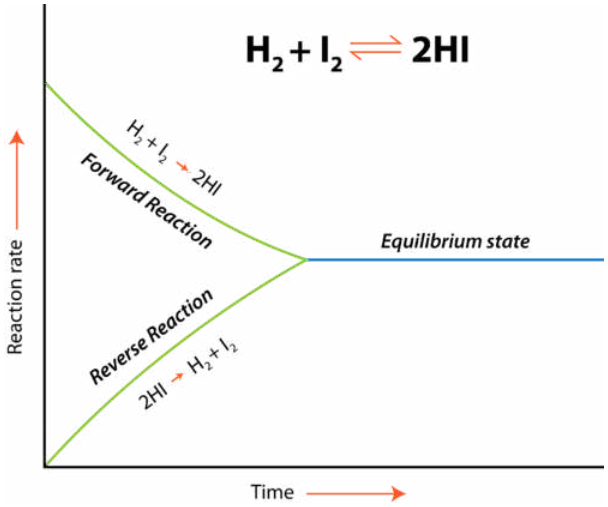


Figure 9.5.1: Equilibrium in reaction: $\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. The figure below shows changes in concentration of $\mathrm{H_2}$, $\mathrm{I_2}$, and HI for two different reactions. In the reaction depicted by the graph on the left (A), the reaction begins with only $\mathrm{H_2}$ and $\mathrm{I_2}$ present. There is no HI initially. As the reaction proceeds towards equilibrium, the concentrations of the $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually decrease, while the concentration of the HI gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. At equilibrium, concentrations of all substances are constant.

In reaction B, the process begins with only HI and no $\mathrm{H_2}$ or $\mathrm{I_2}$. In this case, the concentration of HI gradually decreases while the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of HI at equilibrium is significantly higher than the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$. This is true whether the reaction began with all reactants or all products. The position of equilibrium is a property of the particular reversible reaction and does not depend upon how equilibrium was achieved.

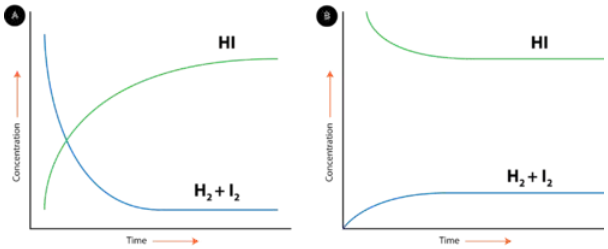


Figure 9.5.2: Equilibrium between reactants and products is achieved regardless of whether the reaction starts with the reactants or products.

Conditions for Equilibrium and Types of Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both forward and reverse are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

The description of equilibrium in this concept refers primarily to equilibrium between reactants and products in a chemical reaction. Other types of equilibrium include phase equilibrium and solution equilibrium. A phase equilibrium occurs when a substance is in equilibrium between two states. For example, a stoppered flask of water attains equilibrium when the rate of evaporation is equal to the rate of condensation. A solution equilibrium occurs when a solid substance is in a saturated solution. At this point, the rate of dissolution is equal to the rate of recrystallization. Although these are all different types of transformations, most of the rules regarding equilibrium apply to any situation in which a process occurs reversibly.



Figure **9.1.3**: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

Red blood cells transport oxygen to the tissues so they can function. In the absence of oxygen, cells cannot carry out their biochemical responsibilities. Oxygen moves to the cells attached to hemoglobin, a protein found in the red cells. In cases of carbon monoxide poisoning, CO binds much more strongly to the hemoglobin, blocking oxygen attachment and lowering the amount of oxygen reaching the cells. Treatment involves the patient breathing pure oxygen to displace the carbon monoxide. The equilibrium reaction shown below illustrates the shift toward the right when excess oxygen is added to the system:

$$\mathrm{Hb(CO)_4}\,(aq) + 4\mathrm{O_2}\,(g) \rightleftharpoons \mathrm{Hb(O_2)_4}\,(aq) + 4\mathrm{CO}\,(g)$$

Equilibrium Constant

Consider the hypothetical reversible reaction in which reactants **A** and **B** react to form products **C** and **D**. This equilibrium can be shown below, where the lowercase letters represent the coefficients of each substance.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentration for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** (K_{eq}) is the ratio of the mathematical product of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{eq} = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units ($\mathrm{mol/L}$).

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the above section, the position of equilibrium for a given reaction does not depend on the starting concentrations and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

The equilibrium constant can vary over a wide range of values. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reducing agent and Cl_2 is a good oxidizing agent, the reaction proceeds essentially to completion.

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad K = 1.6 \times 10^{33} \text{ at } 300\text{K}$$

In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants. An example is the decomposition of water. No wonder you won't find water a very good source of oxygen gas and hydrogen gas at ordinary temperatures!

$$H_2O_{(g)} \rightleftharpoons H_{2(g)} + \tfrac{1}{2}O_{2(g)} \quad K = 8 \times 10^{-41} \text{ at } 25^\circ\text{C}$$

Figure 9.1.4 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products.

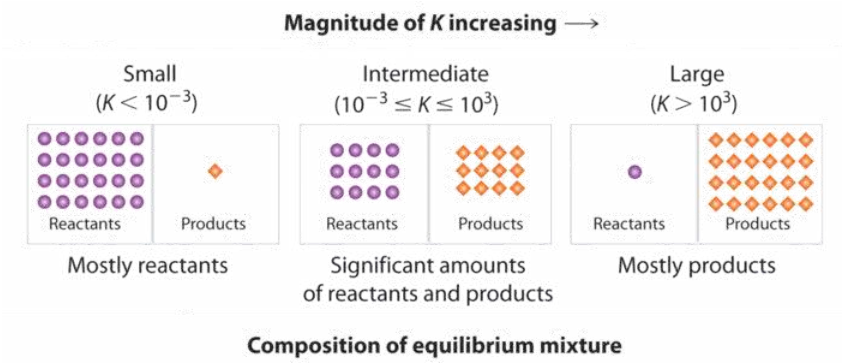


Figure 9.1.4: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

- When K is a very **large** number, the reaction is essentially irreversible, products predominate at equilibrium.
- When K is between 1 and 1000, more products than reactants are present at equilibrium
- When K is between 1 and 0.001, more reactants than products are present at equilibrium.
- When K is a very **small** number, the reaction produces almost no products; only reactants are present at equilibrium.

✔ Example 9.1.1

Write the expression for the equilibrium constant K for the following reaction:

$N_2\ (g) + 3\ H_2\ (g) \rightleftarrows 2\ NH_3\ (g)$

Solution

The equilibrium constant equation is the ratio of the concentration of the products (NH_3) to the concentration of the reactants (N_2 and H_2), each raised to the power of its coefficient in the balanced chemical equation.

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

9.1.1 Exercise

Write the expression of the equilibrium constant K for the following reaction:.

$2\ NOCl\ (g) \rightleftarrows 2\ NO\ (g) + Cl_2\ (g)$

Answer

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

✔ Example 9.1.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Solution

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

9.1.2 Exercise

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. At which temperature would you expect to find the highest proportion of ammonia in the equilibrium mixture?

Answer

a. 327°C, where K is smallest

b. 25°C

Reaction Quotient

The reaction quotient, Q, is used when questioning if we are at equilibrium. The calculation for Q is **exactly** the same as for K but we can only use K when we know we are at equilibrium. Comparing Q and K allows the direction of the reaction to be predicted.

- Q = K equilibrium
- Q < K reaction proceeds to the right to form more products and decrease amount of reactants so value of Q will increase
- Q > K reaction proceeds to the left to form more reactants and decrease amount of products so value of Q will decrease

Key Takeaway

- As a chemical change proceeds, the quantities of the reactants/products will decrease, and those of the products/reactants will increase. Eventually the reaction slows down and the composition of the system stops changing. At this point the reaction is in its *equilibrium state*, and no further change in composition will occur as long as the system is left undisturbed.

Contributors and Attributions

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9.2: Le Châtelier's Principle

Learning Outcomes

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

Original Equilibrium	**Favored Reaction**	**Result**	
$\mathrm{A} \rightleftharpoons \mathrm{B}$	Forward: $\mathrm{A} \rightarrow \mathrm{B}$	[A] decreases; [B] increases	(9.2.1)
$\mathrm{A} \rightleftharpoons \mathrm{B}$	Reverse: $\mathrm{A} \leftarrow \mathrm{B}$	[A] increases; [B] decreases	



Figure 9.2.1: Henri Le Chatelier.

Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightleftharpoons 2\mathrm{NH_3}\,(g) \tag{9.2.2}$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more $\mathrm{N_2}$ is added, the forward reaction will be favored because the forward reaction uses up $\mathrm{N_2}$ and converts it to $\mathrm{NH_3}$. The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more $\mathrm{NH_3}$ is produced. The concentration of $\mathrm{NH_3}$ increases, while the concentrations of $\mathrm{N_2}$ and $\mathrm{H_2}$ decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more $\mathrm{N_2}$ is added, a new equilibrium is achieved by the system. The new concentration of $\mathrm{NH_3}$ is higher because of the favoring of the forward reaction. The new concentration of the $\mathrm{H_2}$ is lower .The concentration of $\mathrm{N_2}$ is higher than in the original equilibrium, but went down slightly following the addition of the $\mathrm{N_2}$ that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_{eq}, does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more $\mathrm{NH_3}$ were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of $\mathrm{NH_3}$ would result in increased formation of the reactants, $\mathrm{N_2}$ and $\mathrm{H_2}$.

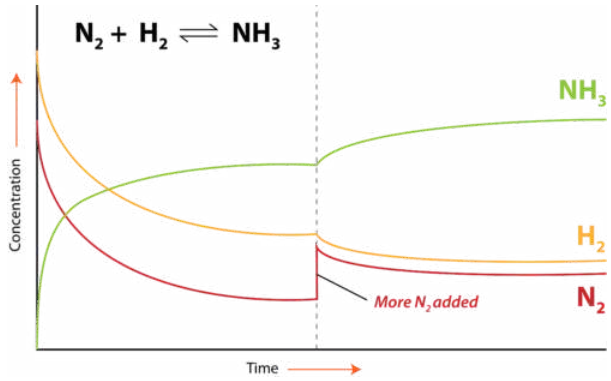


Figure 9.2.2: The Haber-Bosch process is an equilibrium between reactants $\mathbf{N_2}$ and $\mathbf{H_2}$ and product $\mathbf{NH_3}$.

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, $\mathbf{NH_3}$ is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more $\mathbf{NH_3}$ is produced. The concentrations of $\mathbf{N_2}$ and $\mathbf{H_2}$ decrease. Continued removal of $\mathbf{NH_3}$ will eventually force the reaction to go to completion until all of the reactants are used up. If either $\mathbf{N_2}$ or $\mathbf{H_2}$ were removed from the equilibrium system, the reverse reaction would be favored and the concentration of $\mathbf{NH_3}$ would decrease.

The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 9.2.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).

$$\mathbf{N_2}\,(g) + 3\mathbf{H_2}\,(g) \rightleftharpoons 2\mathbf{NH_3}\,(g) + 91\ \mathbf{kJ} \tag{9.2.3}$$

The forward reaction is the exothermic direction: the formation of $\mathbf{NH_3}$ releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as $\mathbf{NH_3}$ decomposes to $\mathbf{N_2}$ and $\mathbf{H_2}$, heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of $\mathbf{NH_3}$ will increase and the amount of $\mathbf{N_2}$ and $\mathbf{H_2}$ will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq} is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

Le Chatelier's principle as related to temperature changes can be illustrated easily be the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.

$$\mathbf{N_2O_4}\,(g) + \mathbf{heat} \rightleftharpoons 2\mathbf{NO_2}\,(g) \tag{9.2.4}$$

Dinitrogen tetroxide (N_2O_4) is colorless, while nitrogen dioxide (NO_2) is dark brown in color. When N_2O_4 breaks down into NO_2, heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

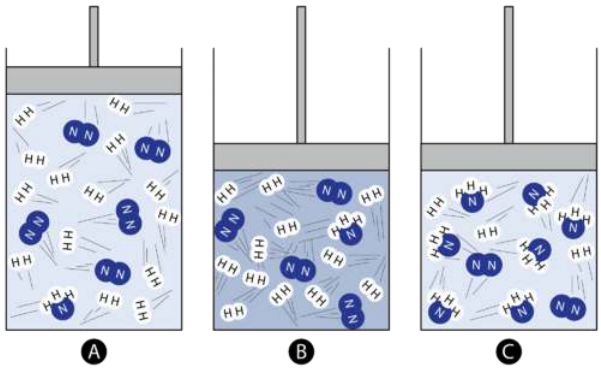


Figure **9.2.3**: Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.

On the far left, the reaction system contains primarily N_2 and H_2, with only one molecule of NH_3 present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more NH_3 is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which NH_3 decomposes to N_2 and H_2. This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

Table **9.2.2**

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + O_2\,(g) \tag{9.2.5}$$

Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of $CaCO_3$ because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of HCl from H_2 and Cl_2.

$$H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2HCl\,(g) \tag{9.2.6}$$

Contributors and Attributions

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9.3: The Effect of a Volume Change on Equilibrium

Changing the pressure or volume of a container enclosing an equilibrium system will only affect the reaction if gases are present.

You may remember from earlier chemistry classes that equal volumes of gases contain an equal number of particles and, under standard conditions of temperature and pressure (STP), one mole of gas occupies a volume of 22.4 L. This is known as the molar volume of gases. So, two moles of any gas will occupy a volume of 44.8 L and one-half mole would occupy 11.2 L.

How does changing pressure and volume affect equilibrium systems?

- If you increase the pressure of a system at equilibrium (typically by reducing the volume of the container), the stress will best be reduced by reaction that favors the side with the ***fewest*** moles of gas, since fewer moles will occupy the smallest volume.
- Conversely, if you decrease the pressure (by increasing the volume of the container), equilibrium will shift to favor the side with the ***most*** moles of gas, since more moles will occupy a greater volume.
- If both sides of the equation have the same number of moles of gas, then there will be no change in the position of equilibrium.

When considering the effect of changing volume or pressure on equilibrium systems, be sure to only count the number of moles of **gases** on each side of the equation. Solids, liquids, and aqueous solutions will not be affected by changing pressure and volume.

Example 9.3.1

Predict the effect on equilibrium when the pressure is increased for the following reaction:

$$\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

Solution

The reactant side of the equation has 1 mole of a gas; the product side has 2 moles. Increasing the pressure favors the side with the fewest moles of gas, so the equilibrium will shift to the left (the reverse reaction will be favored).

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9.4: The Path of a Reaction and the Effect of a Catalyst

The addition of a catalyst to an equilibrium system is a final stress factor. We consider how adding a catalyst affects the following:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Adding a catalyst to this, or any other equilibrium system, will ***not*** affect the position of an equilibrium. A catalyst speeds up both the forward and the reverse reactions, so there is no uneven change in reaction rates. Generally, a catalyst will help a reaction to reach the point of equilibrium *sooner*, but it will not affect the equilibrium otherwise.

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CHAPTER OVERVIEW

10: Redox Chemistry

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The rusting of an old car. A burning campfire. A toy battery-operated car. The chemical processes in your body that break down carbohydrates to produce water, carbon dioxide and energy. The ripening of fruit. It's not easy to see what all of these types of reactions have in common, but they all belong to a very important category of chemical reactions known as oxidation-reduction (or redox) reactions.

10.1: Oxidation and Reduction- Four Views
10.2: Oxidizing and Reducing Agents
10.3: Oxygen - An Abundant and Essential Oxidizing Agent
10.4: Balancing Redox Equations
10.5: Corrosion and Explosion
10.6: Batteries- Using Chemistry to Generate Electricity
10.7: Electrolysis- Using Electricity to Do Chemistry
10.8: Oxidations, Reduction, and Living Things

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10.1: Oxidation and Reduction- Four Views

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Oxygen is an element that has been known for centuries. In its pure elemental form, oxygen is highly reactive, and it readily makes compounds with most other elements. It is also the most abundant element by mass in the Earth's crust. The class of reactions called oxidation and reduction were originally defined with respect to the element oxygen.

Many elements simply combine with oxygen to form the oxide of that element. Heating magnesium in air allows it to combine with oxygen to form magnesium oxide.

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

Many compounds react with oxygen as well, often in very exothermic processes that are generally referred to as combustion reactions. For example, when methane burns, carbon dioxide and water are produced.

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

Carbon dioxide is an oxide of carbon, while water is an oxide of hydrogen. Early scientists viewed oxidation as a process in which a substance was reacted with oxygen to produce one or more oxides. In the previous examples, magnesium and methane are being oxidized.

The definitions of oxidation and reduction were eventually broadened to include similar types of reactions that do not necessarily involve oxygen. Oxygen is more electronegative than any element except for fluorine. Therefore, when oxygen is bonded to any element other than fluorine, electrons from the other atom are shifted away from that atom and toward the oxygen atom. An **oxidation-reduction reaction** (sometimes abbreviated as a **redox reaction**) *is a reaction that involves the full or partial transfer of electrons from one reactant to another*. **Oxidation** *involves a full or partial loss of electrons*, while **reduction** *involves a full or partial gain of electrons*.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The **oxidation number** is a positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction. In oxidation-reduction processes, the driving force for chemical change is in the exchange of electrons between chemical species. A series of rules have been developed to help us.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.
   Examples: H_2, Br_2, Na, Be, K, O_2, P_4, all have oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge.
   Example: In $MgCl_2$, magnesium has an oxidation number of +2, while each chlorine atom has an oxidation number of −1
3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number [except in peroxide compounds (where it is −1) and in binary compounds with fluorine (where it is positive)]; and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion (H^-), in which case rule 2 prevails].

Example: In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound.

4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).
   Example: In SO_2. Each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Note

Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.

Example 10.1.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $CaCl_2$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
3. The Ca^{2+} ion has an oxidation number of +2 by rule 2. Also according to rule 2, each chlorine atom is assigned an oxidation number of −1.

Exercise 10.1.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer

H: +1; O: −2; P: +5

Oxidation and Reduction Reactions

The processes of oxidation and reduction are commonly viewed in terms of the gain or loss of electrons or the increase or decrease in oxidation numbers. However, many reactions in organic chemistry that involve the gain or loss of oxygen or hydrogen are also considered as redox reactions.

The table below summarizes the processes of oxidation and reduction.

Table **10.1.1** The Processes of Oxidation and Reduction.

Oxidation	Reduction
Complete loss of electrons (ionic reaction)	Complete gain of electrons (ionic reaction)
Increase in oxidation number	Decrease in oxidation number
Gain of oxygen	Loss of oxygen
Loss of hydrogen in a molecular compound	Gain of hydrogen in a molecular compound

1. Oxidation is complete loss of electrons. Reduction is complete gain of electrons

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction.

Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, the reaction below represents when acid is added to zinc metal.

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)}$$

zinc atoms are oxidized to Zn^{2+}. The half reaction for the oxidation reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance: the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced reduction half reaction is as follows:

$$\mathrm{2\,H^+ + 2\,e^- \longrightarrow H_2}$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

Note: "LEO says GER"

LEO stands for Losing Electrons is Oxidation, while GER stands for Gaining Electrons is Reduction.



Figure 10.1.1

This guy knows his redox reactions.

2. Oxidation is an increase in oxidation number. Reduction is a decrease in oxidation number.

Consider the reaction below between elemental iron and copper sulfate:

$$\mathrm{Fe + CuSO_4 \rightarrow FeSO_4 + Cu}$$

In the course of the reaction, the oxidation number of Fe increases from zero to $+2$. The oxidation number of copper decreases from $+2$ to 0. This result is in accordance with the activity series. Iron is above copper in the series, so will be more likely to form $\mathrm{Fe^{2+}}$ while converting the $\mathrm{Cu^{2+}}$ to metallic copper $(\mathrm{Cu^0})$.

3. Oxidation is gain of oxygen. Reduction is loss of oxygen.

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of oxidation was “adding oxygen,” so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for reduction: if a molecule loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde ($\mathit{CH3CHO}$) molecule takes on an oxygen atom to become acetic acid ($\mathrm{CH_3COOH}$).

$$\mathrm{2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH}$$

Thus, acetaldehyde is being oxidized.

4. Oxidation is loss of hydrogen in a molecular compound. Reduction is gain of hydrogen in a molecular compound.

Oxidation and reduction can be defined in terms of the gain or loss of hydrogen atoms. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol CH_3CHO, hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

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

Example 10.1.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \rightarrow NH_3$
b. $CH_3CH_2OHCH_3 \rightarrow CH_3COCH_3$
c. $HCHO \rightarrow HCOOH$

Solution

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Exercise 10.1.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \rightarrow CO_2 + H_2O$
b. $NO_2 \rightarrow N_2$
c. $CH_2{=}CH_2 \rightarrow CH_3CH_3$

Answers

a. oxidation
b. reduction
c. reduction

Example 10.1.3:

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

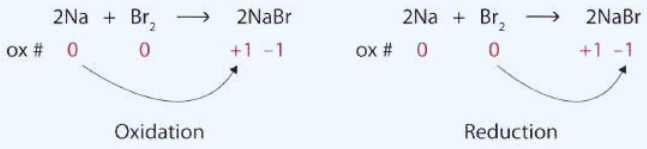
$$\mathbf{2\,Na + Br_2 \longrightarrow 2\,NaBr}$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Example **10.1.3**

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

Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

? Exercise 10.1.3

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

$$C + O_2 \longrightarrow CO_2$$

Answer

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

✔ Example 10.1.4: Gain or Loss of Electrons

For each half reaction, identify if there was a loss or gain of electrons.

a. $2N^{3-} \rightarrow N_2$
b. $Cr^{6+} \rightarrow Cr^{3+}$

Solutions

a. When we compare the overall charges on each side of the equation, we find a charge of 2(-3)=-6 on the left but a charge of 0 on the right. This equation is not properly balanced. To balance it, six electrons must be added on the right side as follows:

$$\ce{2N^{3-} -> N2 + 6e^{-}}\nonumber$$

So there was a *loss of six electrons*. Now the equation is balanced, not only in terms of elements but also in terms of charge.

b. When we compare the overall charges on each side of the equation, we find a charge of +6 on the left and a charge of +3 on the right. This equation is not properly balanced. To end up with an oxidation number of +3 on the right side 3 electrons must be added on the left side as follows:

$$\ce{Cr^{6+} + 3e^{-} -> Cr^{3+}}\nonumber$$

So there was a *gain of three electrons*. Now the equation is balanced in terms of charge.

? Exercise 10.1.4 Gain or Loss of Electrons

For each half reaction, identify if there was a loss or gain of electrons.

a. $O_2 \rightarrow 2O^{2-}$
b. $Cu^{+} \rightarrow Cu^{2+}$

Answers

a. gain of four electrons

b. loss of one electron

Example 10.1.5: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products.

Solution

We start by using symbols of the elements and ions to represent the reaction:

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

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

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

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

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

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

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

Example **10.1.5** Silver reduction reaction

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

Exercise 10.1.5

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products.

Summary

- Rules for determining oxidation numbers are listed.
- Examples of oxidation number determinations are provided.
- Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions.
- Oxidation is defined in terms of the loss of electrons, gain of oxygen, loss of hydrogen, or an increase in oxidation number.
- Reduction is defined in terms of gain of electrons, loss of oxygen, gain of hydrogen, or a decrease in oxidation number.
- Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

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10.2: Oxidizing and Reducing Agents

Learning Objective

- Identify oxidizing and reducing agents.

Life on planet Earth is a complicated and well-organized set of processes. Animals are designed to breathe oxygen and plants are designed to produce oxygen. Photosynthesis is the means by which we get the oxygen we need for life. Light striking a plant pigment known as chlorophyll initiates a complex series of reactions, many of which involve redox processes complete with movement of electrons. In this series of reactions, water is converted to oxygen gas, and we have something to sustain our lives.

The reaction below is a redox reaction that produces zinc sulfide:

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

The half-reactions can be written:

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

In the reaction above, zinc is being oxidized by losing electrons. However, there must be another substance present that gains those electrons and in this case that is the sulfur. In other words, the sulfur is causing the zinc to be oxidized. Sulfur is called the oxidizing agent. The zinc causes the sulfur to gain electrons and become reduced and so the zinc is called the reducing agent. The **oxidizing agent** is a substance that causes oxidation by accepting electrons; therefore, its oxidation state decreases. The **reducing agent** is a substance that causes reduction by losing electrons; therefore its oxidation state increases. The simplest way to think of this is that the oxidizing agent is the substance that is reduced, while the reducing agent is the substance that is oxidized as shown in Figure **10.2.1** and summarized in Table **10.2.1**.

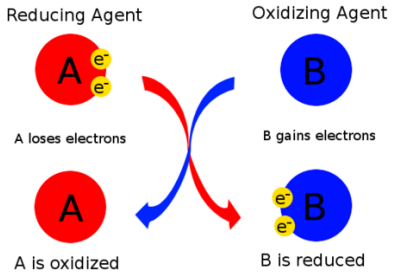


Figure **10.2.1** A reducing agent is oxidized and an oxidizing agent is reduced.

Note

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

Table **10.2.1**: A Comparison of Oxidizing and Reducing Agents.

	Oxidizing Agents	Reducing Agents
Oxidation State	Decreases	Increases
# of Electrons	Gained	Lost
Substance is...	Reduced	Oxidized

The examples below show how to analyze a redox reaction and identify oxidizing and reducing agents.

Example 10.2.1 Half-equations

When chlorine gas is bubbled into a solution of sodium bromide, a reaction occurs which produces aqueous sodium chloride and bromine. Determine what is being oxidized and what is being reduced. Identify the oxidizing and reducing agents.

$$\mathrm{Cl_2\,(g) + 2NaBr\,(aq) \rightarrow 2NaCl\,(aq) + Br_2\,(l)}$$

Solution:

Step 1: Plan the problem.

Break the reaction down into a net ionic equation and then into half-reactions. The substance that loses electrons is being oxidized and is the reducing agent. The substance that gains electrons is being reduced and is the oxidizing agent.

Step 2: Solve.

$$\mathrm{Cl_2\,(g) + \cancel{2Na^+\,(aq)} + 2Br^-\,(aq) \rightarrow \cancel{2Na^+\,(aq)} + 2Cl^-\,(aq) + Br_2\,(l)}$$

$$\mathrm{Cl_2\,(g) + 2Br^-\,(aq) \rightarrow 2Cl^-\,(aq) + Br_2\,(l) \quad (net\ ionic\ equation)}$$

$$\mathrm{Reduction:\ Cl_2\,(g) + 2e^- \rightarrow 2Cl^-\,(aq)}$$
$$\mathrm{Oxidation:\ 2Br^-\,(aq) \rightarrow Br_2\,(l) + 2e^-}$$

The $\mathrm{Cl_2}$ is being reduced and is the oxidizing agent. The $\mathrm{Br^-}$ is being oxidized and is the reducing agent.

Exercise 10.2.1 : Half-equations

Write the following reaction in the form of half-equations. Identify each half-equation as an oxidation or a reduction. Also identify the oxidizing agent and the reducing agent in the overall reaction

$$\mathrm{Zn + 2\,Fe^{3+} \longrightarrow Zn^{2+} + 2\,Fe^{2+}}$$

Answer

The half-equations are

$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$ oxidation—loss of electrons

$\mathrm{2\,e^- + 2\,Fe^{3+} \longrightarrow 2\,Fe^{2+}}$ reduction—gain of electrons

Zinc has been oxidized, the oxidizing *agent* must have been the other reactant, namely, iron(III).

Iron(III) ion has been reduced, the zinc must be the reducing agent.

Example 10.2.2: Identify reducing and oxidizing agents

Identify the reducing and oxidizing agents in the balanced redox reaction:

$$\mathrm{Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)}$$

Oxidation half reaction

$$\mathrm{2Br^-(aq) \rightarrow Br_2(aq)}$$

Oxidation States: -1 to 0

Reduction Half Reaction

$$\mathrm{Cl_2(aq) \rightarrow 2Cl^-(aq)}$$

Oxidation States: 0 to -1

Overview

- $\mathrm{Br^-}$ *loses* an electron; it is *oxidized* from $\mathrm{Br^-}$ to $\mathrm{Br_2}$; thus, $\mathrm{Br^-}$ is the *reducing agent*.
- $\mathrm{Cl_2}$ *gains* one electron; it is *reduced* from $\mathrm{Cl_2}$ to 2 $\mathrm{Cl^-}$; thus, $\mathrm{Cl_2}$ is the *oxidizing agent.*

? Exercise 10.2.2: Identify reducing and oxidizing agents

Identify the oxidizing agent and the reducing agent in the following redox reaction:

$$MnO_4^- + SO_3^{2-} \rightarrow Mn^{2+} + SO_4^{2-}$$

Solution

S is the reducing agent and Mn is the oxidizing agent.

Summary

- An oxidizing agent is a substance that causes oxidation by accepting electrons; therefore, it gets reduced.
- A reducing agent is a substance that causes reduction by losing electrons; therefore it gets oxidized.
- Examples of how to identify oxidizing and reducing agents are shown.

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10.3: Oxygen - An Abundant and Essential Oxidizing Agent

Learning Objectives

- Know the occurrence and properties of oxygen.
- Know reactions involving oxygen as an oxidizing agent.

Elemental oxygen is a strong oxidizing agent. It reacts with most other elements and many compounds. Oxygen was isolated by Michael Sendivogius before 1604, but it is commonly believed that the element was discovered independently by Carl Wilhelm Scheele, in Uppsala, in 1773 or earlier, and Joseph Priestley in Wiltshire, in 1774. The name oxygen was coined in 1777 by Antoine Lavoisier, who first recognized oxygen as a chemical element and correctly characterized the role it plays in combustion.

Oxygen: Occurrence and Properties

By mass, oxygen is the third-most abundant element in the universe, after hydrogen and helium. Oxygen is the most abundant element on the earth's crust. About 50% of the mass of the earth's crust consists of oxygen (combined with other elements, principally silicon). Oxygen occurs as O_2 molecules and, to a limited extent, as O_3 (ozone) molecules in air. It forms about 20% of the mass of the air. About 89% of water by mass consists of combined oxygen. In combination with carbon, hydrogen, and nitrogen, oxygen is a large part of plants and animals.

Oxygen is a colorless, odorless, and tasteless gas at ordinary temperatures. It is slightly denser than air. Although it is only slightly soluble in water (49 mL of gas dissolves in 1 L at STP), oxygen's solubility is very important to aquatic life.

Oxygen is essential in combustion processes such as the burning of fuels. All combustion reactions are also examples of redox reactions. A combustion reaction occurs when a substance reacts with oxygen to create heat. One example is the combustion of octane, the principle component of gasoline:

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \longrightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g)$$

Combustion reactions are a major source of energy for modern industry. Plants and animals use the oxygen from the air in respiration. The administration of oxygen-enriched air is an important medical practice when a patient is receiving an inadequate supply of oxygen because of shock, pneumonia, or some other illness.

The chemical industry employs oxygen for oxidizing many substances. A significant amount of oxygen produced commercially is important in the removal of carbon from iron during steel production. Large quantities of pure oxygen are also necessary in metal fabrication and in the cutting and welding of metals with oxyhydrogen and oxyacetylene torches. Liquid oxygen is important to the space industry. It is an oxidizing agent in rocket engines. It is also the source of gaseous oxygen for life support in space.

As we know, oxygen is very important to life. The energy required for the maintenance of normal body functions in human beings and in other organisms comes from the slow oxidation of chemical compounds. Oxygen is the final oxidizing agent in these reactions. In humans, oxygen passes from the lungs into the blood, where it combines with hemoglobin, producing oxyhemoglobin. In this form, blood transports the oxygen to tissues, where it is transferred to the tissues. The ultimate products are carbon dioxide and water. The blood carries the carbon dioxide through the veins to the lungs, where the blood releases the carbon dioxide and collects another supply of oxygen. Digestion and assimilation of food regenerate the materials consumed by oxidation in the body; the energy liberated is the same as if the food burned outside the body.

Oxygen: Reactions with Other Elements

Oxygen reacts directly at room temperature or at elevated temperatures with all other elements except the noble gases, the halogens, and few second- and third-row transition metals of low reactivity (those with higher reduction potentials than copper). Rust is an example of the reaction of oxygen with iron. The more active metals form peroxides or superoxides. Less active metals and the nonmetals give oxides. Two examples of these reactions are:

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

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

The oxides of halogens, at least one of the noble gases, and metals with higher reduction potentials than copper do not form by the direct action of the elements with oxygen.

Oxygen: Reaction with Compounds

Elemental oxygen also reacts with some compounds. If it is possible to oxidize any of the elements in a given compound, further oxidation by oxygen can occur. For example, hydrogen sulfide, H_2S, contains sulfur with an oxidation state of 2−. Because the sulfur does not exhibit its maximum oxidation state, we would expect H_2S to react with oxygen. It does, yielding water and sulfur dioxide. The reaction is:

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

It is also possible to oxidize oxides such as CO and P_4O_6 that contain an element with a lower oxidation state. The ease with which elemental oxygen picks up electrons is mirrored by the difficulty of removing electrons from oxygen in most oxides. Of the elements, only the very reactive fluorine can oxidize oxides to form oxygen gas.

Most nonmetals react with oxygen to form nonmetal oxides. Depending on the available oxidation states for the element, a variety of oxides might form. Fluorine will combine with oxygen to form fluorides such as OF_2, where the oxygen has a 2+-oxidation state.

Sulfur Oxygen Compounds

The two common oxides of sulfur are sulfur dioxide, SO_2, and sulfur trioxide, SO_3. The odor of burning sulfur comes from sulfur dioxide. Sulfur dioxide, occurs in volcanic gases Figure **10.3.1** and in the atmosphere near industrial plants that burn fuel containing sulfur compounds.



Figure **10.3.1**: Mount Mayon volcano (Philippines) erupting in the early morning of January 23, 2018. (CC BY-SA 4.0; Ezra Acayan via Wikipedia)

Ozone: Another Form of Oxygen

When dry oxygen is passed between two electrically charged plates, ozone (O_3, illustrated in Figure **10.3.2**), an allotrope of oxygen possessing a distinctive odor, forms. The formation of ozone from oxygen is an endothermic reaction, in which the energy comes from an electrical discharge, heat, or ultraviolet light:

$$3\,O_2(g) \xrightarrow{\text{electric discharge}} 2\,O_3(g)$$

The sharp odor associated with sparking electrical equipment is due, in part, to ozone.

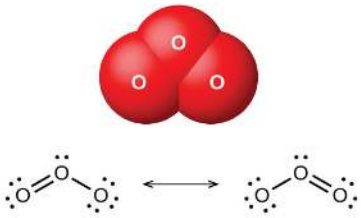


Figure **10.3.2** The image shows the bent ozone (O3) molecule and the resonance structures necessary to describe its bonding.

Ozone forms naturally in the upper atmosphere by the action of ultraviolet light from the sun on the oxygen there. Most atmospheric ozone occurs in the stratosphere, a layer of the atmosphere extending from about 10 to 50 kilometers above the earth's surface. This ozone acts as a barrier to harmful ultraviolet light from the sun by absorbing it via a chemical decomposition reaction:

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

The reactive oxygen atoms recombine with molecular oxygen to complete the ozone cycle. The presence of stratospheric ozone decreases the frequency of skin cancer and other damaging effects of ultraviolet radiation. It has been clearly demonstrated that chlorofluorocarbons, CFCs (known commercially as Freons), which were present as aerosol propellants in spray cans and as refrigerants, caused depletion of ozone in the stratosphere. This occurred because ultraviolet light also causes CFCs to decompose, producing atomic chlorine. The chlorine atoms react with ozone molecules, resulting in a net removal of O_3 molecules from stratosphere. This process is explored in detail in our coverage of chemical kinetics. There is a worldwide effort to reduce the amount of CFCs used commercially, and the ozone hole is already beginning to decrease in size as atmospheric concentrations of atomic chlorine decrease. While ozone in the stratosphere helps protect us, ozone in the troposphere is a problem. This ozone is a toxic component of photochemical smog.

The uses of ozone depend on its reactivity with other substances. It can be used as a bleaching agent for oils, waxes, fabrics, and starch: It oxidizes the colored compounds in these substances to colorless compounds. It is an alternative to chlorine as a disinfectant for water.

Low level ozone (or tropospheric ozone) is an atmospheric pollutant.[42] It is not emitted directly by car engines or by industrial operations, but formed by the reaction of sunlight on air containing hydrocarbons and nitrogen oxides that react to form ozone directly at the source of the pollution or many kilometers down wind.

Ozone reacts directly with some hydrocarbons such as aldehydes and thus begins their removal from the air, but the products are themselves key components of smog.

Ozone can be used to remove iron and manganese from water, forming a precipitate which can be filtered:

$$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3(s) + O_2 + 4H^+$$

$$2Mn^{2+} + 2O_3 + 4H_2O \rightarrow 2MnO(OH)_2(s) + 2O_2 + 4H^+$$

Ozone will also oxidize dissolved hydrogen sulfide in water to sulfurous acid:

$$3O_3 + H_2S \rightarrow H_2SO_3 + 3O_2$$

These three reactions are central in the use of ozone based well water treatment.

Ozone will also detoxify cyanides by converting them to cyanates.

$$CN^- + O_3 \rightarrow CNO^- + O_2$$

Ozone will also completely decompose urea:

$$(NH_2)_2CO + O_3 \rightarrow N_2 + CO_2 + 2H_2O$$

Other Common Oxidizing Agents

Chlorine is usually used (in the form of hypochlorous acid) to kill bacteria and other microbes in drinking water supplies and public swimming pools. In most private swimming pools, chlorine itself is not used, but rather sodium hypochlorite, formed from chlorine and sodium hydroxide, or solid tablets of chlorinated isocyanurates. The drawback of using chlorine in swimming pools is that the

chlorine reacts with the proteins in human hair and skin. The distinctive 'chlorine aroma' associated with swimming pools is not the result of chlorine itself, but of chloramine, a chemical compound produced by the reaction of free dissolved chlorine with amines in organic substances. As a disinfectant in water, chlorine is more than three times as effective against Escherichia coli as bromine, and more than six times as effective as iodine. Increasingly, chloramine itself is being directly added to drinking water for purposes of disinfection, a process known as chloramination.

It is often impractical to store and use poisonous chlorine gas for water treatment, so alternative methods of adding chlorine are used. These include hypochlorite solutions, which gradually release chlorine into the water, and compounds like sodium dichloro-s-triazinetrione (dihydrate or anhydrous), sometimes referred to as "dichlor", and trichloro-s-triazinetrione, sometimes referred to as "trichlor". These compounds are stable while solid and may be used in powdered, granular, or tablet form. When added in small amounts to pool water or industrial water systems, the chlorine atoms hydrolyze from the rest of the molecule forming hypochlorous acid (HOCl), which acts as a general biocide, killing germs, micro-organisms, algae, and so on.

Breathalizers

The breathalyzer is a redox reaction. When the potassium dichromate reacts with ethanol it loses an oxygen atom (gets reduced), going from the orange dichromate to the green chromium sulfate. At the same time dichromate is being reduced, ethanol gains an oxygen atom (gets oxidized), forming acetic acid. The sulfuric acid helps to remove the ethanol from the exhaled air into the test solution and also provides the necessary acidic conditions.

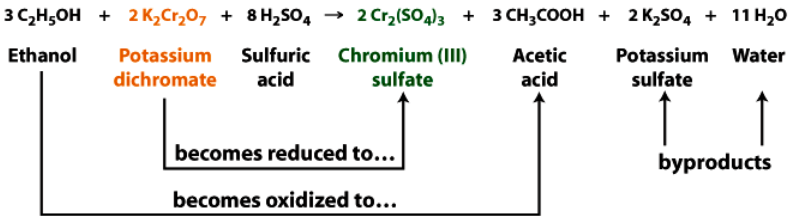


Figure **10.3.3** In this reaction, the chromium atom is reduced from Cr^{6+} to Cr^{3+}, and the ethanol is oxidized to acetic acid.

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

Hydrogen peroxide can be used for the sterilization of various surfaces, including surgical tools and may be deployed as a vapor (VHP) for room sterilization. H_2O_2 demonstrates broad-spectrum efficacy against viruses, bacteria, yeasts, and bacterial spores. In general, greater activity is seen against Gram-positive than Gram-negative bacteria; however, the presence of catalase or other peroxidases in these organisms can increase tolerance in the presence of lower concentrations. Higher concentrations of H_2O_2 (10 to 30%) and longer contact times are required for sporicidal activity.

Hydrogen peroxide is seen as an environmentally safe alternative to chlorine-based bleaches, as it degrades to form oxygen and water and it is generally recognized as safe as an antimicrobial agent by the U.S. Food and Drug Administration (FDA).

Historically hydrogen peroxide was used for disinfecting wounds, partly because of its low cost and prompt availability compared to other antiseptics. It is now thought to inhibit healing and to induce scarring because it destroys newly formed skin cells. Only a very low concentration of

H_2O_2 can induce healing, and only if not repeatedly applied. Surgical use can lead to gas embolism formation. Despite this, it is still used for wound treatment in many countries but is also prevalent as a major first aid antiseptic in the United States

Diluted H_2O_2 (between 1.9% and 12%) mixed with aqueous ammonia is used to bleach human hair. The chemical's bleaching property lends its name to the phrase "peroxide blonde". Hydrogen peroxide is also used for tooth whitening. It can be found in most whitening toothpastes.



Figure 10.3.3: Skin shortly after exposure to 35% H_2O_2. (Public Domain; Olli Niemitalo via Wikipedia)

Almost all applications of potassium permanganate ($KMnO_4$) exploit its oxidizing properties. As a strong oxidant that does not generate toxic byproducts, $KMnO_4$ has many niche uses. Potassium permanganate is used for a number of skin conditions. This includes fungal infections of the foot, impetigo, pemphigus, superficial wounds, dermatitis, and tropical ulcers. It is on the WHO Model List of Essential Medicines, the most important medications needed in a basic health system. Potassium permanganate is used extensively in the water treatment industry.

Benzoyl peroxide (BPO) is a medication and industrial chemical. As a medication, it is used to treat mild to moderate acne. For more severe cases, it may be used with other treatments. Some versions are sold mixed with antibiotics such as clindamycin. Other uses include bleaching flour, hair bleaching, teeth whitening, and textile bleaching.[5] It is also used in the plastic industry

Sodium hypochlorite is most often encountered as a pale greenish-yellow dilute solution commonly known as liquid bleach or simply bleach, a household chemical widely used (since the 18th century) as a disinfectant or a bleaching agent. The compound in solution is unstable and easily decomposes, liberating chlorine, which is the active principle of such products. Indeed, sodium hypochlorite is the oldest and still most important chlorine-based bleach.

Warning

While sodium hypochlorite is non-toxic, its corrosive properties, common availability, and reaction products make it a significant safety risk. In particular, mixing liquid bleach with other cleaning products, such as acids or ammonia, may produce toxic fumes.

Summary

- Oxygen is one of the most reactive elements. This reactivity, coupled with its abundance, makes the chemistry of oxygen very rich and well understood.
- Many compounds of the representative metals and non metals react with oxygen to form oxides.
- Other than oxygen, ozone, chlorine, potassium dichromate, hydrogen peroxide, potassium peroxide, benzoyl peroxide, sodium hypochlorite are common oxidizing agents mentioned in this section, that have many beneficial uses.

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10.4: Balancing Redox Equations

Balancing Redox Equations Using Half-Reactions

Another way to balance redox reactions is by the half-reaction method. This technique involves breaking an equation into its two separate components—the oxidation reaction and the reduction reaction. Since neither oxidation nor reduction can actually occur without the other, we refer to the separate equations as **half-reactions**.

The general technique involves the following:

- The overall equation is broken down into **two** half-reactions. If there are any spectator ions, they are removed from the equations.
- Each half-reaction is balanced separately, first for atoms and then for charge. Electrons are added to one side of the equation or the other in order to balance charge. For example, if the reactant side of the equation has a total charge of +3, the product side must also equal +3.
- Next, the two equations are compared to make sure electrons lost equal electrons gained. One of the half reactions will be an oxidation reaction, the other will be a reduction reaction.
- Finally, the two half-reactions are added together, and any spectator ions that were removed are placed back into the equation.

Consider the following reaction:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

In this reaction, Mg is oxidized and Cl is reduced. You may find it useful to use oxidation numbers to help you determine this. Mg changes from 0 to +2; Cl changes from 0 to -1.

When we write the half-reactions, we break apart compounds that contain either of the key elements (elements undergoing oxidation or reduction). Oxidation numbers are written as if they were ion charges. Notice that the chlorine from $MgCl_2$ is written as two separate ions, not combined, as is Cl_2. Balance the two reactions for atoms.

$Mg \rightarrow Mg^{+2}$	$Cl_2 \rightarrow 2\ Cl^-$

Next balance the equations for charge by adding electrons. Remember, one half-reaction will be an oxidation reaction (electrons on the product side) and the other will be reduction (electrons will be on the reactant side).

$Mg \rightarrow Mg^{+2} + 2\ e^-$	$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$
oxidation	**reduction**

In this example, balancing for charge results in both sides, of both equations, having net charges of 0. That won't always be the case. Be sure you see in this example how charges are balanced.

We then compare the two equations for numbers of electrons. We see that both equations have 2 electrons so we do not need to make any adjustments for that. Finally, add the two equations together:

$$Mg + Cl_2 \rightarrow Mg^{+2} + 2Cl^-$$

and reform any compounds broken apart in the earlier steps:

$$Mg + Cl_2 \rightarrow MgCl_2$$

We see that the original equation was already balanced, not just for atoms, but for electrons as well.

Example 2

$$Cu_{(s)} + AgNO_{3(aq)} \rightarrow Cu(NO_3)2(aq) + Ag_{(s)}$$

Solution

Identify the elements undergoing oxidation (Cu) and reduction (Ag). The nitrate group (NO_3) is a spectator ion which we will not include in our half-reactions.

$Cu \rightarrow Cu^{+2} + 2\ e^-$	$Ag^+ + 1\ e^- \rightarrow Ag$
oxidation	**reduction**

After balancing for atoms and for charge, we see that the two equations do not have the same number of electrons—there are 2 in the copper reaction, but only one in the silver reaction. Multiply everything in the silver reaction by 2, then we will add the equations together:

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions	**Balance electrons**	**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2\ e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2\ e^-}$
$Ag + 1\ e^- \rightarrow Ag^-$	× 2	$2\ Ag^+ + \cancel{2e^-} \rightarrow 2\ Ag$
Add equations together		$Cu + 2\ Ag^+ \rightarrow Cu^{+2} + 2\ Ag$
Reform compound/return spectator ions		**$Cu + 2\ AgNO_3 \rightarrow Cu(NO_3)_2 + 2\ Ag$**

Here is a reaction occurring in an acid solution, which accounts for the presence of the H^+ions. This example adds a little more complexity to our problem.

$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

In this example, spectator ions have already been removed. Even though hydrogen and oxygen do not undergo changes in oxidation number, they are not spectators, and we need to work with them in our half-reactions.

We determine that Mn undergoes reduction (+7 to +2) while Fe undergoes oxidation (+2 to +3). The iron half-reaction is straight forward, but the manganese reaction is more complex—we must include hydrogen and oxygen in its half-reaction:

$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$
oxidation	**reduction**

To balance the manganese half-reaction, first balance for Mn and O atoms. Next balance the H atoms, and finally add enough electrons to balance the charge on both sides of the equation. Be sure you see what has been done, so that you can do it on your own.

Step 1	Step 2	Step 3
Write the balanced half-reactions		**Add half-reactions**
$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	× 5	$5Fe^{2+} \rightarrow 5Fe^{+3} + \cancel{5e^-}$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		$MnO_4^- + 8\,H^+ + \cancel{5e^-} \rightarrow Mn^{2+} + 4\,H_2O$
Add equations together		**$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightarrow Mn^{2+} + 5\,Fe^{3+} + 4H_2O$**

Example 3

$$HNO_3 + Cu + H^+ \rightarrow NO_2 + Cu^{2+} + H_2O$$

Solution

1. Determine what is oxidized, what is reduced, and write the two **balanced** half-reactions (Step 1).
2. Balance for electrons lost = electrons gained (Step 2).
3. Add equations together.

Step 1	Step 2	Step 3
Write the balanced half-reactions		**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2e^-}$
$HNO_3 + H^+ + 1\,e^- \rightarrow NO_2 + H_2O$	× 2	$2HNO_3 + 2H^+ + \cancel{2e^-} \rightarrow 2NO_2 + 2H_2O$
Add equations together		**$2HNO_3 + Cu + 2H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O$**

When balancing redox reactions, either the oxidation number method or the half-reaction method may be used. Often you'll find that one method works best for some equations, while the other method is more suited for other reactions. Or you may find one method just easier to use. The practice exercises and assignments tell you which method to use for a reaction, but as you get get more experience you'll be able to make your own decision as to which method to use.

Writing half-reactions, however, is a skill you will need for our final topic in this course—Electrochemistry—so be sure you can write balanced half-reactions.

Check your understanding with the practice questions, set 3, then complete Assignment 2 .

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10.5: Corrosion and Explosion

Learning Objectives

- Understand the process of corrosion.
- Understand the process of explosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion.

Explosions can occur in nature due to a large influx of energy. Most natural explosions arise from volcanic processes of various sorts. Chemical explosions, usually involve a rapid and violent oxidation reaction that produces large amounts of hot gas. Gunpowder was the first explosive to be discovered and put to use. Other notable early developments in chemical explosive technology were Frederick Augustus Abel's development of nitrocellulose in 1865 and Alfred Nobel's invention of dynamite in 1866. Chemical explosions (both intentional and accidental) are often initiated by an electric spark or flame in the presence of oxygen. Accidental explosions may occur in fuel tanks, rocket engines, etc.

The Rusting of Iron

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

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

The electrons reduce oxygen in the air in acidic solutions.

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

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

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

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

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

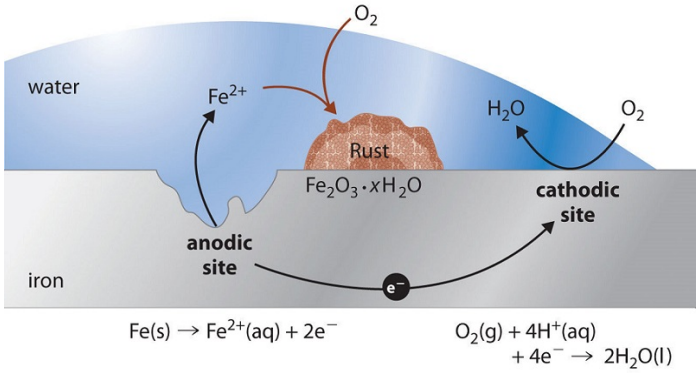


Figure **10.5.1** Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe2+(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal.

One way to keep iron from corroding is to keep it painted. Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active

metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathbf{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

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

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

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the $\mathbf{CuO}$.

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

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

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

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed elsewhere.



Figure **10.5.2**: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Silver Tarnishes

Even though coinage metals are known to be resistant to oxygen in air, silver will tarnish due to $\mathbf{H_2S\,(g)}$

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

Explosive Reactions

TNT is one of the most commonly used explosives for military, industrial, and mining applications. TNT has been used in conjunction with hydraulic fracturing, a process used to recover oil and gas from shale formations. The technique involves displacing and detonating nitroglycerin in hydraulically induced fractures followed by wellbore shots using pelletized TNT.

TNT is valued partly because of its insensitivity to shock and friction, with reduced risk of accidental detonation compared to more sensitive explosives such as nitroglycerin. TNT melts at 80 °C (176 °F), far below the temperature at which it will spontaneously detonate, allowing it to be poured or safely combined with other explosives. TNT neither absorbs nor dissolves in water, which allows it to be used effectively in wet environments. To detonate, TNT must be triggered by a pressure wave from a starter explosive, called an explosive booster.

Although blocks of TNT are available in various sizes (e.g. 250 g, 500 g, 1,000 g), it is more commonly encountered in synergistic explosive blends comprising a variable percentage of TNT plus other ingredients

Upon detonation, TNT decomposes as follows:

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

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

The reaction is exothermic but has a high activation energy in the gas phase (~62 kcal/mol). The condensed phases (solid or liquid) show markedly lower activation energies of roughly 35 kcal/mol due to unique bimolecular decomposition routes at elevated densities. Because of the production of carbon, TNT explosions have a sooty appearance. Because TNT has an excess of carbon, explosive mixtures with oxygen-rich compounds can yield more energy per kilogram than TNT alone. During the 20th century, amatol, a mixture of TNT with ammonium nitrate was a widely used military explosive.

TNT can be detonated with a high velocity initiator or by efficient concussion. For many years, TNT used to be the reference point for the Figure of Insensitivity. TNT had a rating of exactly 100 on the "F of I" scale. The reference has since been changed to a more sensitive explosive called RDX, which has an F of I rating of 80.

ANFO (or AN/FO, for ammonium nitrate/fuel oil) is a widely used bulk industrial explosive. Its name is commonly pronounced as "an-fo". It consists of 94% porous prilled ammonium nitrate (NH_4NO_3) (AN), which acts as the oxidizing agent and absorbent for the fuel, and 6% number 2 fuel oil (FO). The fuel component of ANFO is typically diesel, but kerosene, coal dust, racing fuel, or even molasses have been used instead. Finely powdered aluminium in the mixture will sensitise it to detonate more readily.

The chemistry of ANFO detonation is the reaction of ammonium nitrate with a long-chain alkane (C_nH_{2n+2}) to form nitrogen, carbon dioxide, and water.

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

In an ideal stoichiometrically balanced reaction, ANFO is composed of about 94.3% AN and 5.7% FO by \(\ce{weight. In practice, a slight excess of fuel oil is added, as underdosing results in reduced performance while overdosing merely results in more post-blast fumes. When detonation conditions are optimal, the aforementioned gases are the only products. In practical use, such conditions are impossible to attain, and blasts produce moderate amounts of toxic gases such as carbon monoxide and nitrogen oxides (NOx).

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

ANFO has found wide use in coal mining, quarrying, metal mining, and civil construction in applications where its low cost and ease of use may outweigh the benefits of other explosives, such as water resistance, oxygen balance, higher detonation velocity, or performance in small-diameter columns. ANFO is also widely used in avalanche hazard mitigation.

Summary

- Corrosion and explosion are two major redox processes.
- Examples of corrosion (metal deterioration) and explosion (using TNT and ANFO) are given.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
- TextMap: Chemistry-A Central Science (Brown et al.)
- Wikipedia

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10.6: Batteries- Using Chemistry to Generate Electricity

Learning Objectives

- Identify the substance being oxidized and the substance being reduced in an oxidation-reduction reaction.
- Identify the anode and the cathode given a diagram of an electrolysis apparatus that includes the compound being electrolyzed.
- Describe how batteries can produce electrical energy.

Electricity is an important form of energy that you use every day. It runs your calculators, cell phones, dishwashers, and watches. This form of energy involves moving electrons through a wire and using the energy of these electrons. Electrochemical cells used for power generation are called batteries. Although batteries come in many different shapes and sizes, there are a few basic types. You won't be required to remember details of the batteries, but some general information and features of each type are presented here. Many important chemical reactions involve the exchange of one or more electrons, and we can use this movement of electrons as electricity; batteries are one way of producing this type of energy. The reactions that drive electricity are called oxidation-reduction (or "redox") reactions.

Oxidation and Reduction

Reactions in which electrons are transferred are called oxidation-reduction (or "redox") reactions. There are two parts to these changes: one atom must lose electrons and another atom must gain them. These two parts are described by the terms "oxidation" and "reduction".

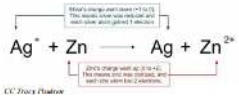
Originally, a substance was said to be oxidized when it reacted with oxygen. Today, the word "oxidized" is still used for those situations, but now we have a much broader second meaning for these words. Today, the broader sense of the word **oxidation** is defined as losing electrons. When a substance loses electrons, its charge will increase. This may feel a bit backwards, but remember that electrons are negative. If an atom loses electrons, it is losing negative particles—so its charge will increase.

The other half of this process, the gaining of electrons, also needs a name. When an atom or an ion gains electrons, the charge on the particle goes down. For example, if a sulfur atom whose charge is zero **(0)** gains two electrons, its charge becomes **(−2)**; if an Fe^{3+} ion gains an electron, its charge changes from **+3** to **+2**. In both cases, the charge on the particle is reduced by the gain of electrons. Remember that electrons have a negative charge, so gaining electrons will result in the charge decreasing. The word **reduction** is defined to mean gaining electrons and the reduction of charge.

In chemical systems, these two processes (oxidation and reduction) must occur simultaneously and the number of electrons lost in the oxidation must be the same as the number of electrons gained in the reduction. In oxidation-reduction reactions, electrons are transferred from one substance to another. Here is an example of an oxidation-reduction reaction:

$$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

In this reaction, the silver ions are gaining electrons to become silver atoms. Therefore, the silver ions are being reduced and the charge of silver is decreasing. The copper atoms are losing electrons to become copper **+2** ions, are therefore being oxidized, and the charge of copper is increasing. Whenever a chemical reaction involves electrons being transferred from one substance to another, the reaction is an **oxidation-reduction reaction** (or a redox reaction).



Half-equations are very helpful in discussing and analyzing processes, but half-reactions cannot occur as they appear. The half-reactions for the reaction above would be:

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Both oxidation and reduction must occur at the same time, so the electrons are donated and absorbed nearly simultaneously. The two half-reactions may be added together to represent a complete reaction. In order to add the half-reactions, the number of electrons donated and the number of electrons accepted must be equal.

Example 9.3.1

For each reaction, identify what is oxidized and what is reduced.

a) $Zn + HCl \rightarrow H_2 + ZnCl_2$

b) $Fe + O_2 \rightarrow Fe_2O_3$

c) $NaBr + I_2 \rightarrow NaI + Br_2$

Solution

In order to determine what is being oxidized and reduced, we must look at charges of atoms and see if they increase or decrease. (Remember, elements have no charge. In a compound, we can use our periodic table and what we learned in Chapter 4 to assign charges.) If the charge increases, the atom was oxidized. If the charge decreases, the atom was reduced.

a) This reaction written with charges is:

$$Zn^0 + H^+Cl^- \rightarrow H_2{}^0 + Zn^{2+}Cl_2{}^-$$

Zn is oxidized because it went from **0** to **+2**. **H** is reduced because it went from **+1** to **0**. **Cl** was neither oxidized nor reduced.

b) This reaction written with charges is:

$$Fe^0 + O_2{}^0 \rightarrow Fe_2{}^{3+}O_3{}^{2-}$$

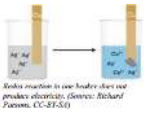
Fe is oxidized because it went from **0** to **+3**. **O** is reduced because it went from **0** to **−2**.

c) This reaction written with charges is:

$$Na^+Br^- + I_2{}^0 \rightarrow Na^+I^- + Br_2{}^0$$

Br is oxidized because it went from **−2** to **0**. **I** is reduced because it went from **0** to **−1**. **Na** was neither oxidized nor reduced as it stayed **+1** the whole time.

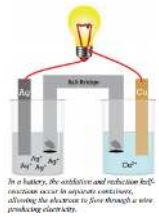
Batteries



Batteries are devices that use chemical reactions to produce electrical energy. These reactions occur because the products contain less potential energy in their bonds than the reactants. The energy produced from excess potential energy not only allows the reaction to occur, but also often gives off energy to the surroundings. Some of these reactions can be physically arranged so that the energy given off is in the form of an electric current. These are the type of reactions that occur inside batteries. When a reaction is arranged to produce an electric current as it runs, the arrangement is called an **electrochemical cell** or a **Galvanic Cell.**

If a strip of copper is placed in a solution of silver nitrate, the following reaction takes place:

$$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$



In this reaction, copper atoms are donating electrons to silver ions, so the silver ions are reduced to silver atoms and copper atoms are oxidized to copper (II) ions.

As the reaction occurs, an observer would see the solution slowly turn blue (Cu^{2+} ions are blue in solution) and a mass of solid silver atoms would build up on the copper strip.

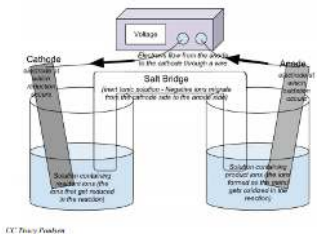
The reaction we just described is not set up in such a way as to produce electricity. It is true that electrons are being transferred, but to produce electricity, we need electrons flowing through a wire so that we can use the energy of these electrons. This reaction, $2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$, is one that could be arranged to produce electricity. To do this, the two half-reactions (oxidation and reduction) must occur in separate compartments, and the separate compartments must remain in contact through an ionic solution and an external wire.

In this electrochemical cell, the copper metal must be separated from the silver ions to avoid a direct reaction. Each electrode in its solution could be represented by a half-reaction.

$$Cu \rightarrow Cu^{2+} + 2e^-$$

$$2Ag^+ + 2e^- \rightarrow 2Ag$$

The wire connects the two halves of the reaction, allowing electrons to flow from one metal strip to the other. In this particular example, electrons will flow from the copper electrode (which is losing electrons) into the silver electrode (which is where the silver ions gain the electrons). The cell produces electricity through the wire and will continue to do so as long as there are sufficient reactants (Ag^+ and Cu) to continue the reaction.



Electrochemical cells will always have two electrodes—the pieces of metal where electrons are gained or lost. (In this example, the strip of Ag metal and Cu metal are the electrodes.) The electrode where reduction occurs and electrons are gained is called the **cathode**. The electrode where oxidation occurs and electrons are lost is called the **anode**. Electrons will always move from the anode to the cathode. The electrons that pass through the external circuit can do useful work such as lighting lights, running cell phones, and so forth.

If the light bulb is removed from the circuit with the electrochemical cell and replaced with a voltmeter, the voltmeter will measure the voltage (electrical potential energy per unit charge) of the combination of half-cells. The size of the voltage produced by a cell depends on the temperature, the metals used for electrodes, and the concentrations of the ions in the solutions. If you increase the concentration of the reactant ion (not the product ion), the reaction rate will increase and so will the voltage.

It may seem complicated to construct an electrochemical cell due to all of their complexities. Electrochemical cells are actually easy to make and sometimes even occur accidentally. If you take two coins of different denomination, push them part way through the peel of a whole lemon, and then connect the two coins with a wire, a small electric current will flow.

1. Primary Batteries (Dry Cell Batteries)

- Non-rechargeable.
- Electrolytes are present as a paste rather than as a liquid.
- General purpose battery used for flashlights, transistor radios, toys, etc.
- The basic dry cell battery consists of: zinc case as the anode (oxidation); a graphite rod as the cathode (reduction) surrounded by a moist paste of either MnO_2, NH_4Cl, and $ZnCl_2$ (or, in alkaline dry cells, a KOH electrolytic paste).
- General reactions for the battery: manganese (IV) oxide-zinc cell (different batteries have different reactions—you don't need to remember any of these reactions).

cathode	$2MnO_{2(s)} + 2\,NH_4^+{}_{(aq)} + 2e^- \rightarrow Mn_2O_{3\,(s)} + H_2O_{(l)} + 2NH_{3\,(aq)}$
anode	$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

- - Maximum voltage of 1.5V. By connecting several cells in a series, 90V can be achieved.
  - Advantages of alkaline batteries: consistent voltage, increased capacity, longer shelf life, and reliable operation at temperatures as low as -40°C.
  - Disadvantage: higher cost.

2. Secondary Batteries (Storage Batteries)

- Rechargeable
- An example: the lead-acid battery used in cars. The anode is a grid of lead-antimony or lead-calcium alloy packed with spongy lead; the cathode is lead (IV) oxide. The electrolyte is aqueous sulfuric acid. This battery consists of numerous small cells connected in parallels (anode to anode; cathode to cathode).
- General reaction:

cathode	$PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4\,(s)} + 2H_2O_{(l)} + 2NH_{3\,(aq)}$
anode	$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4\,(s)} + 2e^-$

- - Secondary batteries are recharged by passing a current through the battery in the opposite direction. In a car battery, this occurs when the engine is running.
  - Other examples include the nickel-iron alkaline battery, nickel-zinc battery, nickel-cadmium alkaline battery, silver-zinc battery, and silver-cadmium battery.

3. Fuel Cells

- Fuel cells are electrochemical cells that convert the energy of a redox combustion reaction directly into electrical energy. Fuel cells require a continuous supply of reactants and a constant removal of products.
- The cathode reactant is usually air or pure oxygen; the anode fuel is a gas such as hydrogen, methane, or propane. Carbon electrodes typically contain a catalyst. The electrolyte is typically KOH.
- General reaction:

cathode	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$
anode	$2H_{2\,(g)} + 4OH^-{}_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
net	$2H_{2\,(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

- Advantages: no toxic waste products (water is the only product); very efficient energy conversion (70-80% efficient).
- Disadvantage: too expensive for large-scale use.

Summary

- A reaction in which there is a transfer of electrons is said to be an oxidation-reduction reaction, or a redox reaction.
- A substance that loses electrons is said to be oxidized, and the substance that gains electrons is said to be reduced.
- Redox reactions can be used in electrochemical cells to produce electricity.
- Electrochemical cells are composed of an anode and cathode in two separate solutions. These solutions are connected by a salt bridge and a conductive wire.
- An electric current consists of a flow of charged particles.
- The electrode where oxidation occurs is called the anode, and the electrode where reduction occurs is called the cathode.

Vocabulary

- **Electrochemical cell** - An arrangement of electrodes and ionic solutions in which a redox reaction is used to make electricity (a battery).
- **Electrolysis** - A chemical reaction brought about by an electric current.
- **Electroplating** - A process in which electrolysis is used as a means of coating an object with a layer of metal.

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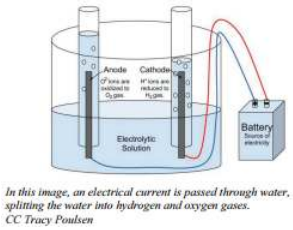
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10.7: Electrolysis- Using Electricity to Do Chemistry

So far, we have discussed how electricity can be produced from chemical reactions in batteries. Some reactions will, instead, use electricity to get a reaction to occur. In these reactions, electrical energy is given to the reactants, causing them to react to form the products. These reactions have many uses. For example, electrolysis is a process that involves forcing electricity through a liquid or solution to cause a reaction to occur. Electrolysis reactions will not run unless energy is put into the system from outside. In the case of electrolysis reactions, the energy is provided by the battery. Think of electrolysis and electrolytic cells as the opposite of electrochemical cells:

	Electrochemical Cells	Electrolytic Cells
Energy conversion	Chemical → Electrical	Electrical → Chemical
Spontaneous chemical reaction?	Yes	No
Value of E°	Positive	Negative

In an electrochemical cell, a spontaneous redox reaction is used to create an electric current; in an electrolytic cell, the reverse will occur—an electric current will be required in order to cause a non-spontaneous chemical reaction to occur. We will look at three examples of the electrolytic process, keeping our discussion on a very basic level—the electrolysis of molten sodium chloride, the electrolysis of water, and electroplating.



In this image, an electrical current is passed through water, splitting the water into hydrogen and oxygen gases.
CC Tracy Poulsen

Figure 16.7.1: An electrical current is passed through water, splitting the water into hydrogen and oxygen gases.

If electrodes connected to battery terminals are placed in liquid sodium chloride, the sodium ions will migrate toward the negative electrode and be reduced while the chloride ions migrate toward the positive electrode and are oxidized. The processes that occur at the electrodes can be represented by what are called half-equations.

Reduction occurs at the positive electrode:

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

Oxidation occurs at the negative electrode:

$$\mathrm{2Cl^- \rightarrow Cl_2 + 2e^-}$$

The overall reaction for this reaction is:

$$\mathrm{2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2}$$

With appropriate treatment from the battery, it is possible to get the metal being reduced in an electrolysis process to adhere strongly to the electrode. The use of electrolysis to coat one material with a layer of metal is called **electroplating**. Usually, electroplating is used to cover a cheap metal with a layer of more expensive and more attractive metal. Many people buy jewelry that is plated in gold. Sometimes, electroplating is used to get a surface metal that is a better conductor of electricity. When you wish to have the surface properties of gold (attractive, corrosion resistant, or good conductor), but you don't want to have the great cost of making an entire object out of solid gold, the answer may be to use cheap metal to make the object and then electroplate a thin layer of gold on the surface.

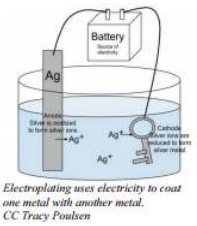


Figure 16.7.2: Silver plating.

To silver plate an object like a spoon (plated silverware is less expensive than pure silver), the spoon is placed in the position of the cathode in an electrolysis set up with a solution of silver nitrate. When the current is turned on, the silver ions will migrate through the solution, touch the cathode (spoon) and adhere to it. With enough time and care, a layer of silver can be plated over the entire spoon. The anode for this operation would often be a large piece of silver, from which silver ions would be oxidized and these ions would enter the solution. This is a way of ensuring a steady supply of silver ions for the plating process.

- Half-reaction at the cathode:

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

- Half-reaction at the anode:

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

Some percentage of the gold and silver jewelry sold is electroplated. The connection points in electric switches are often gold plated to improve electrical conductivity, and most of the chromium pieces on automobiles are chromium plated.

Electrolysis of Molten Sodium Chloride

If we look at the latin roots of the word "electrolysis" we learn that it means, essentially, to "break apart" (*lysis*) using electricity. Our first example of an electrolytic cell will examine how an electric current can be used to break apart an ionic compound into its elements. The following equation represents the breaking apart of $NaCl_{(l)}$:

$2NaCl_{(l)} \rightarrow 2Na_{(l)} + Cl_{2\,(g)}$

The half-reactions involved in this process are:

			E°
reduction	$2Na^+_{(l)} + 2e^- \rightarrow Na_{(s)}$		-2.71 V
oxidation	$Cl^-_{(l)} \rightarrow Cl_{2\,(g)} + 2\,e^-$		-1.36V
	net voltage required		**- 4.07V**

Notice that a negative voltage (-4.07V) results when we add up the half-reactions. This tells us that the overall reaction will **NOT** be spontaneous, and a minimum of 4.07 volts will be required for this reaction to occur.

As we shall see, our set-up will have a number of similarities to our electrochemical cells. We will need electrodes and an electrolyte to carry the electric current.

In our NaCl example, the electrodes will simply carry the current, but otherwise will not be directly involved in the reaction. The electrolyte will be the actual molten (melted) NaCl. The electrodes and electrolyte are both required to carry the electric current. Molten NaCl must be used because solid ionic compounds do not carry an electric charge.

Some key differences with an electrochemical cell set-up:

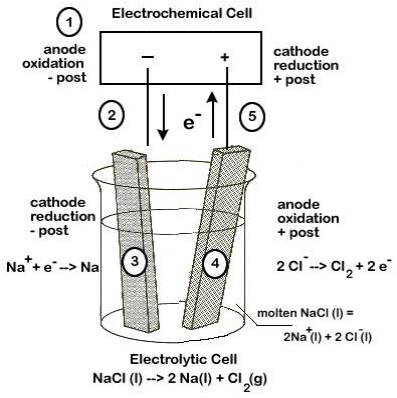
- The two half-reactions are not separated by a salt bridge.
- An electrochemical cell (or other source of electric current) will be required.

Other important items to note:

- The anode of the electrolytic cell is the site of oxidation and the cathode is the site of reduction, just as in an electrochemical cell.
- In an electrochemical cell, the anode is negative and cathode positive, but this is reversed in the electrolytic cell—the anode is positive and the cathode is negative.

Carefully study the diagram of our set up, taking special care to trace the path of the electrons. Unless electrons make a complete circuit, a reaction will not occur.

1. 1. Electrons are "produced" in the battery at the anode, the site of oxidation.
   2. The electrons leave the electrochemical cell through the external circuit.
   3. These negative electrons create a negative electrode in the electrolytic cell, which attracts the positive Na^+ ions in the electrolyte. Na^+ ions combine with the free electrons and become reduced ($2Na^+ + 2e^- \rightarrow Na$).
   4. Meanwhile, the negative Cl^- become attracted to the positive electrode of the electrolytic cell. At this electrode, chlorine is oxidized, releasing electrons ($Cl^- \rightarrow Cl_2 + 2\ e^-$).
   5. These electrons travel through the external circuit, returning to the electrochemical cell.



Electrolysis of Water

Our second example of electrolysis and electrolytic cells involves the breakdown of water. We will find a situation very similar to the electrolysis of molten NaCl. The following equation represents the breaking apart of $H_2O_{(l)}$:

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\ (g)}$

It may be more difficult to predict the half-reactions involved, but they are:

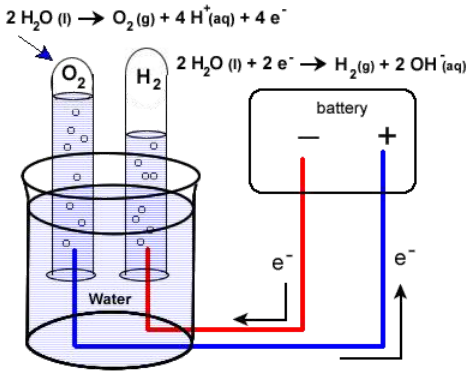
			E°
reduction	$2H_2O_{(l)} + 2e^- \rightarrow H_2 + 2\ OH^-$		-0.83 V
oxidation	$2H_2O_{(l)} \rightarrow O_2 + 4H^+ + 4e^-$		-1.23V
	(see note below for net equation)		
		net voltage required	**- 2.06V**

The set up will be very similar to our last example with some minor differences. Water does not carry a charge well, so an electrolyte is added to the water. Vinegar, a weak acid (acetic acid) may be used. To collect the hydrogen and oxygen gases produced, inverted test tubes are often added, as shown in our diagram below.

Again, take special care to trace the path of the electrons. Unless electrons make a complete circuit, a reaction will not occur.

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2\ OH^-_{(aq)}$

$2H_2O_{(l)} \rightarrow O_{2\,(g)} + 4H^+_{(aq)} + 4e^-$



1. 1. Electrons are "produced" in the battery at the anode, the site of oxidation.
   2. The electrons leave the electrochemical cell through the external circuit.
   3. These negative electrons create a negative electrode in the electrolytic cell which causes the reduction of water.
      Note that the area around this electrode will become basic as OH^- ions are produced.
   4. Meanwhile, the positive electrode water will undergo oxidation.
   5. Electrons produced during this oxidation process will return to the electrochemical cell.

A note about the balanced equation for the electrolysis of water:

You may notice from the half reactions that adding up the equations doesn't initially give us our net equation of:

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\,(g)}$

Once you balance for electrons (multiply the reduction equation by 2), you'll find that the equations actually add up to:

$6H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\,(g)} + 4H^+_{(aq)} + 4\,OH^-_{(aq)}$

The hydrogen and hydroxide ions will combine to form 4 moles of $H_2O_{(l)}$. Finding our net amount of $H_2O_{(l)}$ involved gives us our final equation:

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\,(g)}$

Summary

- Electrochemical cells are composed of an anode and cathode in two separate solutions. These solutions are connected by a salt bridge and a conductive wire.
- An electric current consists of a flow of charged particles.
- The electrode where oxidation occurs is called the anode and the electrode where reduction occurs is called the cathode.
- In electroplating, the object to be plated is made the cathode.

Vocabulary

- **Electrochemical cell** - An arrangement of electrodes and ionic solutions in which a redox reaction is used to make electricity (also known as a battery).
- **Electrolysis** - A chemical reaction brought about by an electric current.
- **Electroplating** - A process in which electrolysis is used as a means of coating an object with a layer of metal.

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10.8: Oxidations, Reduction, and Living Things

Learning Objective

- Know the overall reactions involved in respiration and photosynthesis.

Oxidation and reduction reactions are especially crucial in biological processes such as cellular respiration and photosynthesis.

Cellular respiration is a set of metabolic reactions and processes that take place in the cells of organisms to convert biochemical energy from nutrients into adenosine triphosphate (ATP), and then release waste products. Cellular respiration is considered an exothermic redox reaction which releases heat. The overall reaction occurs in a series of biochemical steps, most of which are redox reactions themselves. Although cellular respiration is technically a combustion reaction, it clearly does not resemble one when it occurs in a living cell because of the slow release of energy from the series of reactions.

Nutrients that are commonly used by animal and plant cells in respiration include sugar, amino acids and fatty acids, and the most common oxidizing agent (electron acceptor) is molecular oxygen (O_2).

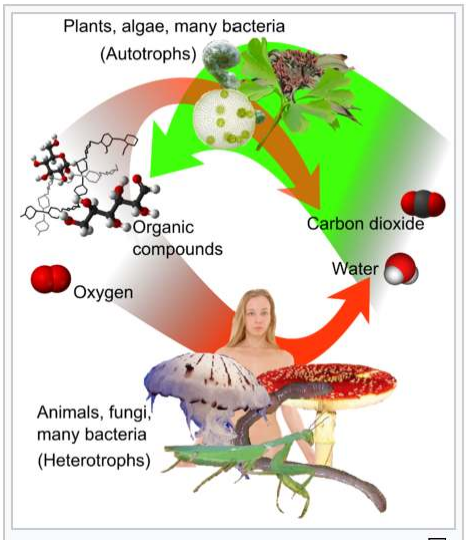


Figure **10.8.1** Aerobic respiration (red arrows) is the main means by which both fungi and animals utilize chemical energy in the form of organic compounds that were previously created through photosynthesis (green arrow). (CC-BY-SA 2.0, Mikael Häggström, Wikimedia)

The reaction for aerobic respiration is essentially the reverse of photosynthesis and is simplified as:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2880kJ/mol$$

Green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called **photosynthesis**, in which carbon dioxide and water are converted to glucose ($\mathbf{C_6H_{12}O_6}$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy

A simplified overall formula for photosynthesis is:

$$6CO_2 + 6H_2O + photons \rightarrow C_6H_{12}O_6 + 6O_2$$

or simply

carbon dioxide + water + sunlight → glucose + oxygen gas

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.

Summary

- Redox reactions are common in organic and biological chemistry, including aerobic respiration, and photosynthesis.

Contributors and Attributions

- Libretext: Basics of GOB Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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CHAPTER OVERVIEW

11: Quantities in Chemical Reactions

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So far, we have talked about chemical reactions in terms of individual atoms and molecules. Although this works, most of the reactions occurring around us involve much larger amounts of chemicals. Even a tiny sample of a substance will contain millions, billions, or a hundred billion billions of atoms and molecules. How do we compare amounts of substances to each other, in chemical terms, when it is so difficult to count to a hundred billion billion? Actually, there are ways to do this, which we will explore in this chapter. In doing so, we will increase our understanding of stoichiometry, which is the study of the numerical relationships between the reactants and the products in a balanced chemical reaction.

11.1: Climate Change - Too Much Carbon Dioxide

11.2: Stoichiometry

11.3: Mole-to-Mole Conversions

11.4: Limiting Reactant and Theoretical Yield

11.5: Making Molecules- Mole to Mass (or vice versa) and Mass-to-Mass Conversions

11.6: Limiting Reactant, Theoretical Yield, and Percent Yield from Initial Masses of Reactants

Template:HideTOC

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11.1: Climate Change - Too Much Carbon Dioxide

Carbon dioxide (CO_2) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. Figure **11.1.1** shows CO_2 levels during the last three glacial cycles, as reconstructed from ice cores.

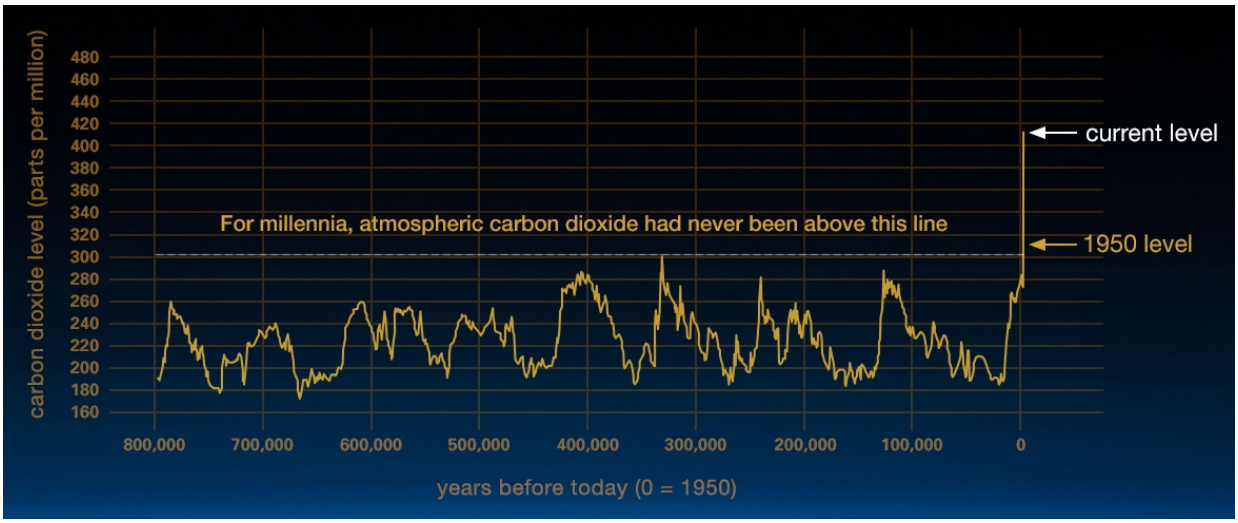


Figure **11.1.1**: This graph, based on the comparison of atmospheric samples contained in ice cores and more recent direct measurements, provides evidence that atmospheric CO2 has increased since the Industrial Revolution. (Luthi, D., et al. 2008; Etheridge, D.M., et al. 2010; Vostok ice core data/J.R.R. Petit et al.; NOAA Mauna Loa CO2 record. NASA.) Line graph of carbon dioxide levels from 800 thousand before up until present day; current carbon dioxide level is higher than all historical levels.

Carbon dioxide (CO_2) is the primary greenhouse gas emitted through human activities. In 2015, CO_2 accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle, both by adding more CO_2 to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO_2 from the atmosphere. While CO_2 emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2. As an example of how CO_2 can be generated, consider the combustion of octane, a component of gasoline:

$$2\,C_8H_{18}\,(l) + 21\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g) \qquad (11.1.1)$$

The balanced reaction in Equation 11.1.1 demonstrates that for every two molecules of octane that are burned, 16 molecules of CO_2 are generated.

Contributions & Attributions

- Earth Science Communications Team at NASA's Jet Propulsion Laboratory, California Institute of Technology
- EPA

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11.2: Stoichiometry

Learning Objectives

- Explain the meaning of the term "stoichiometry".
- Determine the relative amounts of each substance in chemical equations.

You have learned that chemical equations provide us with information about the types of particles that react to form products. Chemical equations also provide us with the relative number of particles and moles that react to form products. In this section you will explore the quantitative relationships that exist between the quantities of reactants and products in a balanced equation. This is known as **stoichiometry**.

Stoichiometry, by definition, is the calculation of the quantities of reactants or products in a chemical reaction using the relationships found in the balanced chemical equation. The word stoichiometry is actually Greek from two words: *στοικηιον*, which means "element", and \(\mu \epsilon \tau \rho \omicron \nu), which means "measure".

Interpreting Chemical Equations

The mole, as you remember, is a quantitative measure that is equivalent to Avogadro's number of particles. So how does this relate to the chemical equation? Look at the chemical equation below.

$$2CuSO_4 + 4KI \rightarrow 2CuI + 2K_2SO_4 + I_2$$

The coefficients used, as we have learned, tell us the relative amounts of each substance in the equation. So for every 2 units of copper (II) sulfate ($CuSO_4$) we have, we need to have 4 units of potassium iodide (KI). For every two dozen copper (II) sulfates, we need 4 dozen potassium iodides. Because the unit "mole" is also a counting unit, we can interpret this equation in terms of moles, as well: For every two moles of copper (II) sulfate, we need 4 moles potassium iodide.

The production of ammonia (NH_3) from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

The balanced equation can be analyzed in several ways, as shown in the figure below.

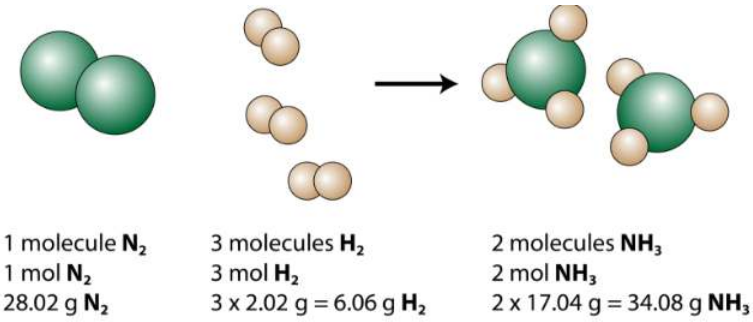


Figure 11.2.1: This representation of the production of ammonia from nitrogen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

We see that 1 molecule of nitrogen reacts with 3 molecules of hydrogen to form 2 molecules of ammonia. This is the smallest possible relative amount of the reactants and products. To consider larger relative amounts, each coefficient can be multiplied by the same number. For example, 10 molecules of nitrogen would react with 30 molecules of hydrogen to produce 20 molecules of ammonia.

The most useful quantity for counting particles is the mole. So if each coefficient is multiplied by a mole, the balanced chemical equation tells us that 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia. This is the conventional way to interpret any balanced chemical equation.

Finally, if each mole quantity is converted to grams by using the molar mass, we can see that the law of conservation of mass is followed. $1\ \text{mol}$ of nitrogen has a mass of $28.02\ \text{g}$, while $3\ \text{mol}$ of hydrogen has a mass of $6.06\ \text{g}$, and $2\ \text{mol}$ of ammonia has a mass of $34.08\ \text{g}$.

$$28.02\ \text{g}\ \text{N}_2 + 6.06\ \text{g}\ \text{H}_2 \rightarrow 34.08\ \text{g}\ \text{NH}_3$$

Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.

Example 11.2.1

The equation for the combustion of ethane (C_2H_6) is

$$2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$$

a. Indicate the number of formula units or molecules in the balanced equation.
b. Indicate the number of moles present in the balanced equation.

Solution

a. Two molecules of C_2H_6 plus seven molecules of O_2 yields four molecules of CO_2 plus six molecules of H_2O.
b. Two moles of C_2H_6 plus seven moles of O_2 yields four moles of CO_2 plus six moles of H_2O.

Exercise 11.2.1

For the following equation below, indicate the number of formula units or molecules, and the number of moles present in the balanced equation.

$$\text{KBrO}_3 + 6\text{KI} + 6\text{HBr} \rightarrow 7\text{KBr} + 3\text{H}_2\text{O}$$

Answer

One molecules of KBrO_3 plus six molecules of KI plus six molecules of HBr yields seven molecules of KBr plus three molecules of I_2 and three molecules of H_2O. One mole of KBrO_3 plus six moles of KI plus six moles of HBr yields seven moles of KBr plus three moles of I_2 plus three moles of H_2O.

Summary

- Stoichiometry is the calculation of the quantities of reactants or products in a chemical reaction using the relationships found in a balanced chemical equation.
- The coefficients in a balanced chemical equation represent the reacting ratios of the substances in the reaction.
- The coefficients of a balanced equation can be used to determine the ratio of moles of all substances in the reaction.

Vocabulary

- **Stoichiometry** - The calculation of quantitative relationships of the reactants and products in a balanced chemical equation.
- **Formula unit** - The empirical formula of an ionic compound.
- **Mole ratio** - The ratio of the moles of one reactant or product to the moles of another reactant or product according to the coefficients in the balanced chemical equation.

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11.3: Mole-to-Mole Conversions

/;Learning Objectives

- Use a balanced chemical equation to determine molar relationships between substances.

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). As follows, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4H_2 + 2O_2 \rightarrow 4H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22H_2 + 11O_2 \rightarrow 22H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ \mathrm{H_2} + 6.022 \times 10^{23}\ \mathrm{O_2} \rightarrow 12.044 \times 10^{23}\ \mathrm{H_2O}$$

These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ mol\ \mathrm{H_2} + 1\ mol\ \mathrm{O_2} \rightarrow 2\ mol\ \mathrm{H_2O}$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

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

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level, but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”

By the same token, the ratios we constructed to describe a molecular reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

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

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

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

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

Example 11.3.1

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

Solution

Solutions to Example 8.3.1

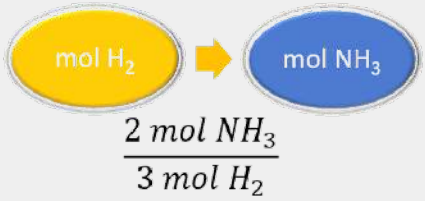
Steps for Problem Solving	How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?
Find a balanced equation that describes the reaction.	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{2}H_2 + O_2 \rightarrow \underline{2}H_2O$
Identify the "given" information and what the problem is asking you to "find."	Given: moles H_2O Find: moles oxygen
List other known quantities.	1 mol O_2 = 2 mol H_2O
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ O_2}{2\ mol\ H_2O}$
Cancel units and calculate.	$\cancel{27.6\ mol\ H_2O} \times \frac{1\ mol\ O_2}{\cancel{2\ mol\ H_2O}} = 13.8\ mol\ O_2$ To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.
Think about your result.	Since each mole of oxygen produces twice as many moles of water, it makes sense that the produced amount is greater than the reactant amount

Example 11.3.2

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

Solution

Solutions to Example 8.3.2

Steps for Problem Solving	How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?
Find a balanced equation that describes the reaction.	Unbalanced: $N_2 + H_2 \rightarrow NH_3$ Balanced: $N_2 + \underline{3}H_2 \rightarrow \underline{2}NH_3$
Identify the "given" information and what the problem is asking you to "find."	Given: $\mathbf{H_2 = 4.20\ mol}$ Find: $\mathbf{mol}$ of $\mathbf{NH_3}$
List other known quantities.	3 mol H_2 = 2 mol NH_3
Prepare a concept map and use the proper conversion factor.	 $\frac{2\ mol\ NH_3}{3\ mol\ H_2}$
Cancel units and calculate.	$\cancel{4.20\ mol\ H_2} \times \frac{2\ mol\ NH_3}{\cancel{3\ mol\ H_2}} = 2.80\ mol\ NH_3$ The reaction of $\mathbf{4.20\ mol}$ of hydrogen with excess nitrogen produces $\mathbf{2.80\ mol}$ of ammonia.
Think about your result.	The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

Exercise 11.3.3

a. Given the following balanced chemical equation:

$$\mathbf{C_5H_{12} + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O}$$

, How many moles of $\mathbf{H_2O}$ can be formed if 0.0652 mol of $\mathbf{C_5H_{12}}$ were to react?

b. Balance the following unbalanced equation and determine how many moles of $\mathbf{H_2O}$ are produced when 1.65 mol of NH_3 react:

$$\mathbf{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

Answer a

0.391 mol H_2O

Answer b

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

Summary

- The balanced chemical reaction can be used to determine molar relationships between substances.

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11.4: Limiting Reactant and Theoretical Yield

Learning Objectives

- Identify the limiting reactant (limiting reagent) in a given chemical reaction.
- Calculate how much product will be produced from the limiting reactant.
- Calculate how much reactant(s) remains when the reaction is complete.

In all examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants were left over at the end of the reaction. This is often desirable—as in the case of a space shuttle—where excess oxygen or hydrogen is not only extra freight to be hauled into orbit, but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely, but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is:

$$\text{1 box mix} + \text{2 eggs} \rightarrow \text{1 batch brownies} \tag{11.4.1}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

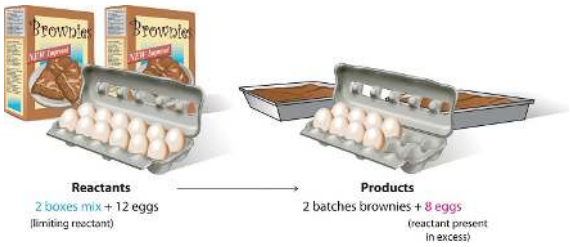
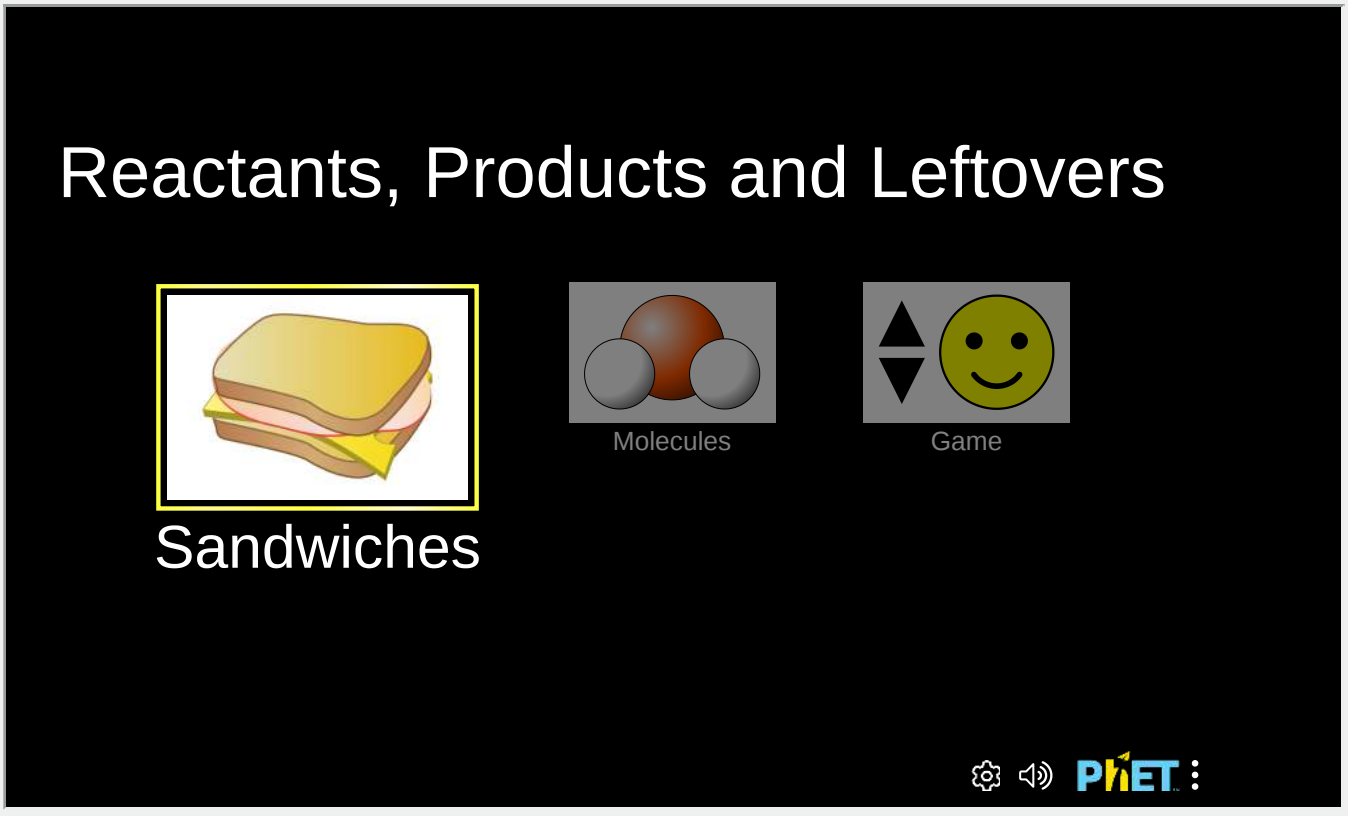


Figure **11.4.1**: The Concept of a Limiting Reactant in the Preparation of Brownies. For a chemist, the **balanced** chemical equation is the recipe that must be followed. 2 boxes of brownie mix and 12 eggs results in 2 batches of brownies and 8 eggs; in this case the 8 eggs are reactant present in excess

PhET Simulation: Reactants, Products and Leftovers

View this interactive simulation illustrating the concepts of limiting and excess reactants.



Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$H_2 + Cl_2(g) \rightarrow 2\,HCl(g)$$

The balanced equation shows that hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the limiting reactant, and the other substance is the excess reactant. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen non-reacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example, in the previous paragraph, complete reaction of the hydrogen would yield:

$$\text{mol HCl produced} = 3\ \text{mol } H_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol } H_2} = 6\ \text{mol HCl}$$

Complete reaction of the provided chlorine would produce:

$$\text{mol HCl produced} = 2\ \text{mol } Cl_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol } Cl_2} = 4\ \text{mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure **11.4.2**).

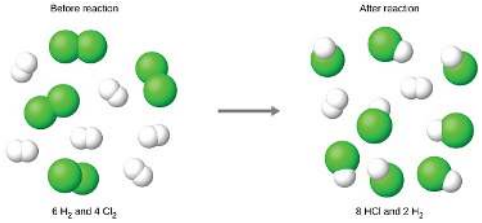


Figure **11.4.2**: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 C l subscript 2." To the right of the reaction arrow, there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the limiting reactant; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reactant and which is in excess.

How to Identify the Limiting Reactant (Limiting Reagent)

There are two ways to determine the limiting reactant. One method is to find and compare the mole ratio of the reactants used in the reaction (Approach 1). Another way is to calculate the grams of products produced from the given quantities of reactants; the reactant that produces the **smallest** amount of product is the limiting reactant (Approach 2). This section will focus more on the second method.

Approach 1 (The "Reactant Mole Ratio Method"): Find the limiting reactant by looking at the number of moles of each reactant.

1. Determine the balanced chemical equation for the chemical reaction.
2. Convert all given information into moles (most likely, through the use of molar mass as a conversion factor).
3. Calculate the mole ratio from the given information. Compare the calculated ratio to the actual ratio.
4. Use the amount of limiting reactant to calculate the amount of product produced.
5. If necessary, calculate how much is left in excess of the non-limiting (excess) reactant.

Approach 2 (The "The Product Method"): Find the limiting reactant by calculating and comparing the amount of product that each reactant will produce.

1. Balance the chemical equation for the chemical reaction.
2. Convert the given information into moles.
3. Use stoichiometry for each individual reactant to find the mass of product produced.
4. The reactant that produces a lesser amount of product is the limiting reactant.
5. The reactant that produces a larger amount of product is the excess reactant.
6. To find the amount of remaining excess reactant, subtract the mass of excess reactant consumed from the total mass of excess reactant given.

The key to recognizing which reactant is the limiting reactant is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reactant. What we need to do is determine an amount of one product (either moles or mass) assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reactant. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

Example **11.4.1**: Identifying the Limiting Reactant

As an example, consider the balanced equation

$$4\,C_2H_3Br_3 + 11\,O_2 \rightarrow 8\,CO_2 + 6\,H_2O + 6\,Br_2$$

What is the limiting reactant if 76.4 grams of $C_2H_3Br_3$ reacted with 49.1 grams of O_2?

Solution

Using Approach 1:

Step 1: ***Balance the chemical equation.***

The equation is already balanced with the relationship

4 mol $C_2H_3Br_3$ to 11 mol O_2 to 6 mol H_2O to 6 mol Br

Step 2: Convert all given information into moles.

$$76.4\ \cancel{\text{g } C_2H_3Br_3} \times \frac{1\ \text{mol } C_2H_3Br_3}{266.72\ \cancel{\text{g } C_2H_3B_3}} = 0.286\ \text{mol } C_2H_3Br_3$$

$$49.1\ \cancel{\text{g } O_2} \times \frac{1\ \text{mol } O_2}{32.00\ \cancel{\text{g } O_2}} = 1.53\ \text{mol } O_2$$

Step 3: Calculate the mole ratio from the given information. Compare the calculated ratio to the actual ratio.

Assuming that all of the oxygen is used up,

$$1.53\ \cancel{\text{mol } O_2} \times \frac{4\ \text{mol } C_2H_3Br_3}{11\ \cancel{\text{mol } O_2}} = 0.556\ \text{mol } C_2H_3Br_3 \text{ are required.}$$

Because 0.556 moles of $C_2H_3Br_3$ required > 0.286 moles of $C_2H_3Br_3$ available, $C_2H_3Br_3$ is the limiting reactant.

Using Approach 2:

Step 1: ***Balance the chemical equation.***

The equation is already balanced with the relationship

4 mol $C_2H_3Br_3$ to 11 mol O_2 to 6 mol H_2O to 6 mol Br_2

Step 2 and Step 3: Convert mass to moles and stoichiometry.

$$76.4\ \cancel{\text{g } C_2H_3Br_3} \times \frac{1\ \cancel{\text{mol } C_2H_3Br_3}}{266.72\ \cancel{\text{g } C_2H_3Br_3}} \times \frac{8\ \cancel{\text{mol } CO_2}}{4\ \cancel{\text{mol } C_2H_3Br_3}} \times \frac{44.01\ \text{g } CO_2}{1\ \cancel{\text{mol } CO_2}} = 25.2\ \text{g } CO_2$$

$$49.1\ \cancel{\text{g } O_2} \times \frac{1\ \cancel{\text{mol } O_2}}{32.00\ \cancel{\text{g } O_2}} \times \frac{8\ \cancel{\text{mol } CO_2}}{11\ \cancel{\text{mol } O_2}} \times \frac{44.01\ \text{g } CO_2}{1\ \cancel{\text{mol } CO_2}} = 49.1\ \text{g } CO_2$$

Step 4: The reactant that produces a smaller amount of product is the limiting reactant.

Therefore, by either method, **$C_2H_3Br_3$** is the limiting reactant.

Example 11.4.2: Identifying the Limiting Reactant and the Mass of Excess Reactant

For example, in the reaction of magnesium metal and oxygen, calculate the mass of magnesium oxide that can be produced if 2.40 g ***Mg*** reacts with 10.0 g ***O_2***. Also determine the amount of excess reactant. **MgO** is the only product in the reaction.

Solution

Following Approach 1:

Step 1: Balance the chemical equation.

$$2\ \text{Mg (s)} + O_2\ \text{(g)} \rightarrow 2\ \text{MgO (s)}$$

The balanced equation provides the relationship of 2 mol Mg to 1 mol O_2 to 2 mol MgO

Step 2 and Step 3: Convert mass to moles and stoichiometry.

$$2.40\ \cancel{\text{g Mg}} \times \frac{1\ \cancel{\text{mol Mg}}}{24.31\ \cancel{\text{g Mg}}} \times \frac{2\ \cancel{\text{mol MgO}}}{2\ \cancel{\text{mol Mg}}} \times \frac{40.31\ \text{g MgO}}{1\ \cancel{\text{mol MgO}}} = 3.98\ \text{g MgO}$$

$$10.0\ \cancel{\text{g } O_2} \times \frac{1\ \cancel{\text{mol } O_2}}{32.00\ \cancel{\text{g } O_2}} \times \frac{2\ \cancel{\text{mol MgO}}}{1\ \cancel{\text{mol } O_2}} \times \frac{40.31\ \text{g MgO}}{1\ \cancel{\text{mol MgO}}} = 25.2\ \text{g MgO}$$

Step 4: The reactant that produces a smaller amount of product is the limiting reactant.

Mg produces less MgO than does O_2 (3.98 g MgO vs. 25.2 g MgO), therefore Mg is the limiting reactant in this reaction.

Step 5: The reactant that produces a larger amount of product is the excess reactant.

O_2 produces more amount of MgO than Mg (25.2g MgO vs. 3.98 MgO), therefore O_2 is the excess reactant in this reaction.

Step 6: Find the amount of remaining excess reactant by subtracting the mass of the excess reactant consumed from the total mass of excess reactant given.

Mass of excess reactant calculated using the limiting reactant:

$$2.40\ \cancel{\text{g Mg}} \times \frac{1\ \cancel{\text{mol Mg}}}{24.31\ \cancel{\text{g Mg}}} \times \frac{1\ \cancel{\text{mol } O_2}}{2\ \cancel{\text{mol Mg}}} \times \frac{32.00\ \text{g } O_2}{1\ \cancel{\text{mol } O_2}} = 1.58\ \text{g } O_2$$

OR

Mass of excess reactant calculated using the mass of the product:

$$3.98\ \cancel{\text{g MgO}} \times \frac{1\ \cancel{\text{mol MgO}}}{40.31\ \cancel{\text{g MgO}}} \times \frac{1\ \cancel{\text{mol } O_2}}{2\ \cancel{\text{mol MgO}}} \times \frac{32.0\ \text{g } O_2}{1\ \cancel{\text{mol } O_2}} = 1.58\ \text{g } O_2$$

Mass of total excess reactant given – mass of excess reactant consumed in the reaction:

10.0g O_2 - (available) 1.58g O_2 (used) = 8.42g O_2 (excess)

Therefore, O_2 is in excess.

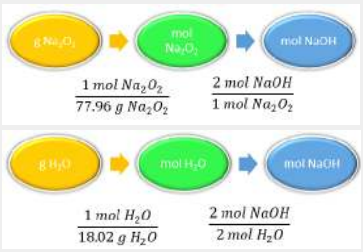
Example 11.4.3: Limiting Reactant

What is the limiting reactant if 78.0 grams of Na_2O_2 were reacted with 29.4 grams of H_2O? The unbalanced chemical equation is

$$Na_2O_2\,(s) + H_2O\,(l) \longrightarrow NaOH\,(aq) + H_2O_2\,(l)$$

Solution

Solutions to Example 8.4.3

Steps for Problem Solving- The Product Method	Example 11.4.1
Identify the "given" information and what the problem is asking you to "find."	Given: 78.0 grams of Na_2O_2 29.4 g H_2O Find: limiting reactant
List other known quantities.	1 mol Na_2O_2= 77.96 g/mol 1 mol H_2O = 18.02 g/mol Since the amount of product in grams is not required, only the molar mass of the reactants is needed.
Balance the equation.	Na_2O_2 (s) + $\underline{2}H_2O$ (l) → $\underline{2}$NaOH (aq) + H_2O_2 (l) The balanced equation provides the relationship of 1 mol Na_2O_2 to 2 mol H_2O 2mol NaOH to 1 mol H_2O_2
Prepare a concept map and use the proper conversion factor.	 Because the question only asks for the limiting reactant, we can perform two **mass-mole** calculations and determine which amount is less.
Cancel units and calculate.	$$78.0\ g\ Na_2O_2 \times \frac{1\ mol\ Na_2O_2}{77.96\ g\ Na_2O_2} \times \frac{2\ mol\ NaOH}{1\ mol\ Na_2O_2} \times \frac{40\ g\ NaOH}{1\ mol\ NaOH} = 2.00\ mol\ NaOH$$ $$29.4\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} \times \frac{2\ mol\ NaOH}{2\ mol\ Na_2O_2} \times \frac{40\ g\ NaOH}{1\ mol\ NaOH} = 1.63\ mol\ NaOH$$ Therefore, H_2O is the *limiting reactant*.

Think about your result.

Example 11.4.4: Limiting Reactant and Mass of Excess Reactant

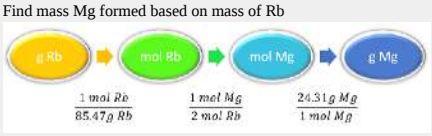
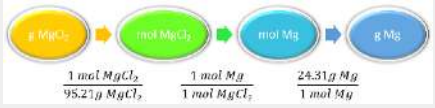
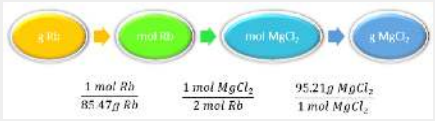
A 5.00 g quantity of **Rb** is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

What mass of **Mg** is formed, and what mass of remaining reactant is left over?

Solution

Solutions to Example 8.4.10

Steps for Problem Solving- The Product Method	Example 11.4.2
Steps for Problem Solving	A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction: $$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$ What mass of Mg is formed, and what mass of remaining reactant is left over?
Identify the "given" information and what the problem is asking you to "find."	Given: 5.00g Rb, 2.44g MgCl2 Find: mass of Mg formed, mass of remaining reactant
List other known quantities.	• molar mass: Rb = 85.47 g/mol • molar mass: $MgCl_2$ = 95.21 g/mol • molar mass: Mg = 24.31 g/mol
Prepare concept maps and use the proper conversion factor.	Find mass Mg formed based on mass of Rb  Find mass of Mg formed based on mass of $MgCl_2$  Conversion factors: 1 mole MgCl2 to 95.21 grams MgCl2, 1 mole Mg to 1 mole MgCl2, 24.31 grams Mg to 1 mole Mg Use limiting reactant to determine amount of excess reactant consumed  Conversion factors: 1 mole Rb to 85.47 grams Rb, 1 mole MgCl2 to 2 moles Rb, 95.21 grams MgCl2 to 1 mole MgCl2
Cancel units and calculate.	Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less. $$5.00\ g\ Rb \times \frac{1\ mol\ Rb}{85.47\ g\ Rb} \times \frac{1\ mol\ Mg}{2\ mol\ Rb} \times \frac{24.31\ g\ Mg}{1\ mol\ Mg} = 0.711\ g\ Mg$$ $$3.44\ g\ MgCl_2 \times \frac{1\ mol\ MgCl_2}{95.21\ g\ MgCl_2} \times \frac{1\ mol\ Mg}{1\ mol\ MgCl_2} \times \frac{24.31\ g\ Mg}{1\ mol\ Mg} = 0.878\ g\ Mg$$ The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reactant. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of $MgCl_2$ reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount. $$5.00\ g\ Rb \times \frac{1\ mol\ Rb}{85.47\ g\ Rb} \times \frac{1\ mol\ MgCl_2}{2\ mol\ Rb} \times \frac{95.21\ g\ MgCl_2}{1\ mol\ MgCl_2} = 2.78\ g\ MgCl_2\ reacted$$ Because we started with 3.44 g of $MgCl_2$, we have 3.44 g $MgCl_2$ − 2.78 g $MgCl_2$ reacted = 0.66 g $MgCl_2$ left
Think about your result.	It usually is not possible to determine the limiting reactant using just the initial masses, as the reagents have different molar masses and coefficients.

? Exercise 11.4.1

Given the initial amounts listed, what is the limiting reactant, and what is the mass of the leftover reactant?

$$\underset{MgO(s)}{22.7\ g} + \underset{H_2S}{17.9\ g} \rightarrow MgS(s) + H_2O(l)$$

Answer

H_2S is the limiting reagent; 1.5 g of MgO are left over.

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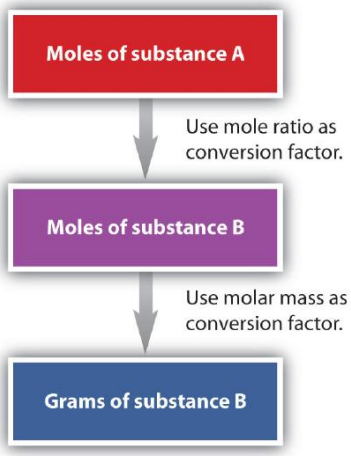
11.5: Making Molecules- Mole to Mass (or vice versa) and Mass-to-Mass Conversions

Learning Objectives

- Convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

Mole to Mass Conversions

We have established that a balanced chemical equation is balanced in terms of moles, as well as atoms or molecules. We have used balanced equations to set up ratios, in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions—such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that relation to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations. Flowchart of mole mass calculations: To convert from moles of substance A to moles of substance B, use the mole ratio conversion factor, and to convert from moles to grams of substance B, use molar mass conversion factor

As an example, consider the balanced chemical equation

$$\mathrm{Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3} \tag{11.5.1}$$

If we have 3.59 mol of $\mathrm{Fe_2O_3}$, how many grams of $\mathrm{SO_3}$ can react with it? Using the mole-mass calculation sequence, we can determine the required mass of $\mathrm{SO_3}$ in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of $\mathrm{SO_3}$ needed. Then, using the molar mass of $\mathrm{SO_3}$ as a conversion factor, we determine the mass that this number of moles of $\mathrm{SO_3}$ has.

As usual, we start with the quantity we were given:

$$3.59\ \cancel{\mathrm{mol\ Fe_2O_3}} \times \left(\frac{3\ \mathrm{mol\ SO_3}}{1\ \cancel{\mathrm{mol\ Fe_2O_3}}}\right) = 10.77\ \mathrm{mol\ SO_3} \tag{11.5.2}$$

The mol $\mathrm{Fe_2O_3}$ units cancel, leaving mol $\mathrm{SO_3}$ unit. Now, we take this answer and convert it to grams of $\mathrm{SO_3}$, using the molar mass of $\mathrm{SO_3}$ as the conversion factor:

$$10.77\ \cancel{\mathrm{mol\ SO_3}} \times \left(\frac{80.06\ \mathrm{g\ SO_3}}{1\ \cancel{\mathrm{mol\ SO_3}}}\right) = 862\ \mathrm{g\ SO_3} \tag{11.5.3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of $\mathrm{SO_3}$ will react with 3.59 mol of $\mathrm{Fe_2O_3}$. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:

$$3.59\ \cancel{mol\ Fe_2O_3} \times \underbrace{\left(\frac{3\ \cancel{mol\ SO_3}}{1\ \cancel{mol\ Fe_2O_3}}\right)}_{\text{converts to moles of } SO_3} \times \underbrace{\left(\frac{80.06\ g\ SO_3}{1\ \cancel{mol\ SO_3}}\right)}_{\text{converts to grams of } SO_3} = 862\ g\ SO_3$$

We get exactly the same answer when combining all math steps together.

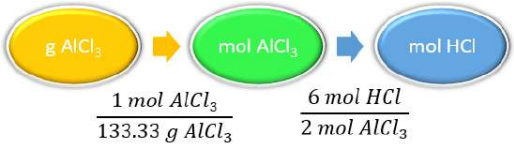
Example 11.5.1: Generation of Aluminum Oxide

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

$$\mathbf{2\,AlCl_3 + 3\,H_2O(\ell) \longrightarrow Al_2O_3 + 6\,HCl\,(g)}$$

Solution

Solutions to Example 8.5.1

Steps for Problem Solving	Example 11.5.1
Identify the "given" information and what the problem is asking you to "find."	Given: 249 g AlCl3 Find: moles HCl
List other known quantities.	1 mol AlCl3 = 133.33 g AlCl3 6 mol of HCl to 2 mol $AlCl_3$
Prepare a concept map and use the proper conversion factor.	 Flowchart of needed conversion factors: 1 mole AlCl3 to 133.33 grams AlCl3, and 6 moles HCl to 2 moles AlCl3
Cancel units and calculate.	$249\ \cancel{g\ AlCl_3} \times \frac{1\ \cancel{mol\ AlCl_3}}{133.33\ \cancel{g\ AlCl_3}} \times \frac{6\ mol\ HCl}{2\ \cancel{mol\ AlCl_3}} = 5.60\ mol\ HCl$
Think about your result.	Since 249 g of $AlCl_3$ is less than 266.66 g, the mass for 2 moles of $AlCl_3$ and the relationship is 6 mol of HCl to 2 mol $AlCl_3$, the answer should be less than 6 moles of HCl.

Exercise 11.5.1: Generation of Aluminum Oxide

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

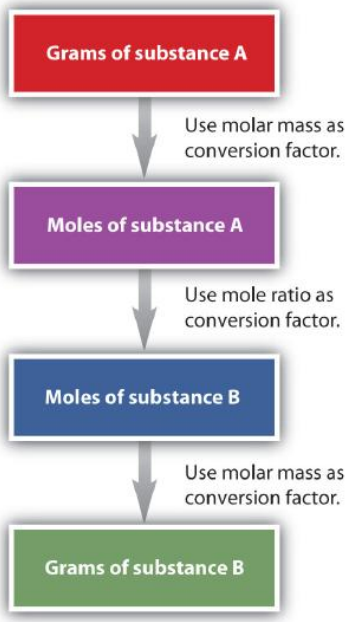
$$\mathbf{2\,AlCl_3 + 3\,H_2O(\ell) \longrightarrow Al_2O_3 + 6\,HCl\,(g)}$$

Answer

0.442 mol Al_2O_3

Mass to Mass Conversions

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques. Flowchart of mole mass calculations: To convert from grams to moles of substance A, use molar mass conversion factor; To convert from moles of substance A to moles of substance B, use the mole ratio conversion factor, and to convert from moles to grams of substance B, use molar mass conversion factor

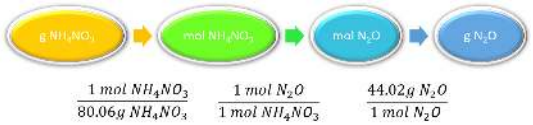
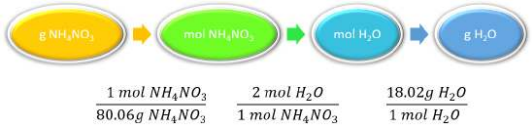
✔ Example 11.5.2: Decomposition of Ammonium Nitrate

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

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

In a certain experiment, $45.7\ \mathrm{g}$ of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Solutions to Example 8.5.2

Steps for Problem Solving	Example 11.5.2
Identify the "given" information and what the problem is asking you to "find."	Given: $45.7\ g\ NH_4NO_3$ Find: Mass $N_2O = ?\ g$ Mass $H_2O = ?\ g$
List other known quantities.	1 mol $NH_4NO_3 = 80.06\ g$ 1 mol $N_2O = 44.02\ g$ 1 mol $H_2O = 18.02\ g$ 1 mol NH_4NO_3 to 1 mol N_2O to 2 mol H_2O
Prepare two concept maps and use the proper conversion factor.	 Flowchart of conversion factors: 1 mole NH4NO3 to 80.06 grams NH4NO3, 1 mole N2O to 1 mole NH4NO3, 44.02 grams N2O to 1 mole N2O  Flowchart of conversion factors: 1 mole NH4NO3 to 80.06 grams NH4NO3, 2 moles H2O to 1 mole NH4NO3, 18.02 grams H2O to 1 mole H2O
Cancel units and calculate.	$45.7\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.06\ g\ NH_4NO_3} \times \frac{1\ mol\ N_2O}{1\ mol\ NH_4NO_3} \times \frac{44.02\ g\ N_2O}{1\ mol\ N_2O} = 25.1\ g\ N_2O$ $45.7\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.06\ g\ NH_4NO_3} \times \frac{2\ mol\ H_2O}{1\ mol\ NH_4NO_3} \times \frac{18.02\ g\ H_2O}{1\ mol\ H_2O} = 20.6\ g\ H_2O$
Think about your result.	The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.

? Exercise 11.5.2: Carbon Tetrachloride

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4\,(g) + 4\,Cl_2\,(g) \longrightarrow CCl_2\,(l) + 4\,HCl\,(l)$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Answer

908.7g HCl

Summary

- Calculations involving conversions between moles of a substance and the mass of that substance can be done using conversion factors.
- A balanced chemical reaction can be used to determine molar and mass relationships between substances.

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11.6: Limiting Reactant, Theoretical Yield, and Percent Yield from Initial Masses of Reactants

Learning Objectives

- Calculate percentage or actual yields from known amounts of reactants.

The world of pharmaceutical production is an expensive one. Many drugs have several steps in their synthesis and use costly chemicals. A great deal of research takes place to develop better ways to make drugs faster and more efficiently. Studying how much of a compound is produced in any given reaction is an important part of cost control.

Percent Yield

Chemical reactions in the real world don't always go exactly as planned on paper. In the course of an experiment, many things will contribute to the formation of less product than predicted. Besides spills and other experimental errors, there are usually losses due to an incomplete reaction, undesirable side reactions, etc. Chemists need a measurement that indicates how successful a reaction has been. This measurement is called the percent yield.

To compute the percent yield, it is first necessary to determine how much of the product should be formed based on stoichiometry. This is called the **theoretical yield**, the maximum amount of product that can be formed from the given amounts of reactants. The **actual yield** is the amount of product that is actually formed when the reaction is carried out in the laboratory. The **percent yield** is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Percent yield is very important in the manufacture of products. Much time and money is spent improving the percent yield for chemical production. When complex chemicals are synthesized by many different reactions, one step with a low percent yield can quickly cause a large waste of reactants and unnecessary expense.

Typically, percent yields are understandably less than 100% because of the reasons indicated earlier. However, percent yields greater than 100% are possible if the measured product of the reaction contains impurities that cause its mass to be greater than it actually would be if the product was pure. When a chemist synthesizes a desired chemical, he or she is always careful to purify the products of the reaction. Example $11.6.1$ illustrates the steps for determining percent yield.

Example 11.6.1: Decomposition of Potassium Chlorate

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below:

$$2KClO_3\,(s) \rightarrow 2KCl\,(s) + 3O_2\,(g)$$

In a certain experiment, $40.0\ g\ KClO_3$ is heated until it completely decomposes. The experiment is performed and the oxygen gas is collected and its mass is found to be $14.9\ g$.

a. What is the theoretical yield of oxygen gas?
b. What is the percent yield for the reaction?

Solution

a. Calculation of theoretical yield

First, we will calculate the theoretical yield based on the stoichiometry.

Step 1: Identify the "given" information and what the problem is asking you to "find".

Given: Mass of $KClO_3 = 40.0\ g$

Mass of O_2 collected = 14.9g

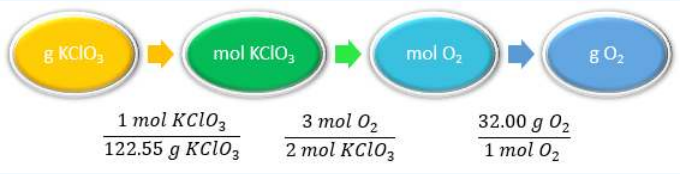
Find: Theoretical yield, g O_2

Step 2: List other known quantities and plan the problem.

1 mol $KClO_3$ = 122.55 g/mol

1 mol O_2 = 32.00 g/mol

Step 3: Apply stoichiometry to convert from the mass of a reactant to the mass of a product:



Step 4: Solve.

$$40.0\ \text{g}\ KClO_3 \times \frac{1\ \text{mol}\ KClO_3}{122.55\ \text{g}\ KClO_3} \times \frac{3\ \text{mol}\ O_2}{2\ \text{mol}\ KClO_3} \times \frac{32.00\ \text{g}\ O_2}{1\ \text{mol}\ O_2} = 15.7\ \text{g}\ O_2$$

The theoretical yield of O_2 is **15.7 g**, 15.67 g unrounded.

Step 5: Think about your result.

The mass of oxygen gas must be less than the **40.0 g** of potassium chlorate that was decomposed.

b. Calculation of percent yield

Now we will use the actual yield and the theoretical yield to calculate the percent yield.

Step 1: Identify the "given" information and what the problem is asking you to "find".

Given: Theoretical yield =15.67 g, use the un-rounded number for the calculation.

Actual yield = 14.9g

Find: Percent yield, % Yield

Step 2: List other known quantities and plan the problem.

No other quantities needed.

Step 3: Use the percent yield equation below.

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Step 4: Solve.

$$\text{Percent Yield} = \frac{14.9\ \text{g}}{15.67\ \text{g}} \times 100\% = 94.9\%$$

Step 5: Think about your result.

Since the actual yield is slightly less than the theoretical yield, the percent yield is just under **100%**.

Example 11.6.2: Oxidation of Zinc

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$

What is the percent yield?

Solution

Solutions to Example 8.6.2

Steps for Problem Solving-The Product Method	Example 11.6.1
Identify the "given" information and what the problem is asking you to "find."	Given: 1.274 g CuSO4 Actual yield = 0.392 g Cu Find: Percent yield
List other known quantities.	1 mol CuSO4= 159.62 g/mol 1 mol Cu = 63.55 g/mol Since the amount of product in grams is not required, only the molar mass of the reactants is needed.
Balance the equation.	The chemical equation is already balanced. The balanced equation provides the relationship of 1 mol CuSO4 to 1 mol Zn to 1 mol Cu to 1 mol ZnSO4.
Prepare a concept map and use the proper conversion factor.	 The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield (g Cu) is found by performing **mass-mass** calculation based on the initial amount of $CuSO_4$.
Cancel units and calculate.	Double subscripts: use braces to clarify Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be: $\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$ $= \left(\frac{0.392\ g\ Cu}{0.5072\ g\ Cu}\right) \times 100$ $= 77.3\%$
Think about your result.	Since the actual yield is slightly less than the theoretical yield, the percent yield is just under **100%**.

Exercise 11.6.1

What is the percent yield of a reaction that produces 12.5 g of the Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$CCl_4 + 2\,HF \rightarrow CF_2Cl_2 + 2\,HCl$$

Answer

48.3%

Summary

Theoretical yield is calculated based on the stoichiometry of the chemical equation. The actual yield is experimentally determined. The percent yield is determined by calculating the ratio of actual yield to theoretical yield.

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CHAPTER OVERVIEW

12: Chemical Bonding

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How do atoms make compounds? Typically they join together in such a way that they lose their identities as elements and adopt a new identity as a compound. These joins are called *chemical bonds*. But how do atoms join together? Ultimately, it all comes down to electrons. Before we discuss how electrons interact, we need to introduce a tool to simply illustrate electrons in an atom.

12.1: Prelude to Chemical Bonds
12.2: Representing Valence Electrons with Dots
12.3: Lewis Structures of Ionic Compounds- Electrons Transferred
12.4: Covalent Lewis Structures- Electrons Shared
12.5: Writing Lewis Structures for Covalent Compounds
12.6: Violations of the Octet Rule
12.7: Resonance - Equivalent Lewis Structures for the Same Molecule
12.8: Predicting the Shapes of Molecules
12.9: Electronegativity and Polarity - Why Oil and Water Don’t Mix

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12.1: Prelude to 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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12.2: Representing Valence Electrons with Dots

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:

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

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 each 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 12.2.1: Lewis Dot Diagrams

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 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 12.2.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a



Answer b



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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12.3: Lewis Structures of Ionic Compounds- Electrons Transferred

Learning Objectives

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

In Section 4.7, we demonstrated that ions are formed by losing electrons to make cations, or by gaining electrons to form anions. The astute reader may have noticed something: many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. The **octet rule** explains the favorable trend of atoms having eight electrons in their valence shell. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

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

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

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



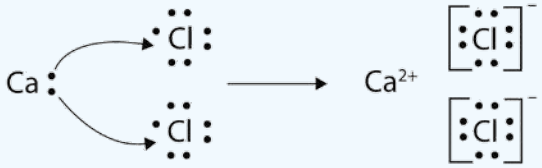
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the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

Example 12.3.1: Synthesis of Calcium Chloride from Elements

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

Solution

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

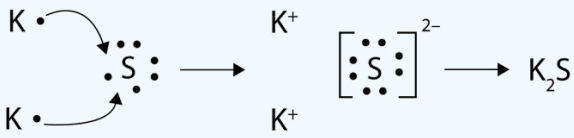


The oppositely charged ions attract each other to make $CaCl_2$.

Exercise 12.3.1

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

Answer



Summary

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

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12.4: Covalent Lewis Structures- Electrons Shared

Learning Objectives

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

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

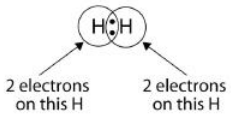
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

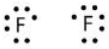
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



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

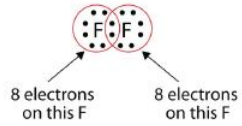
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



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:



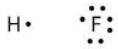
We can also write this using a dash to represent the shared electron pair:



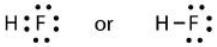
There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F

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:



We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 12.4.1:

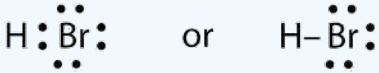
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

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



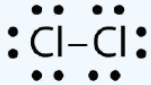
The two atoms can share their unpaired electron:



Exercise 12.4.1

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

Answer



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

Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of $\mathbf{C_2H_4}$. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two } \mathbf{C} \text{ atoms } = 2 \times 4 = 8 \text{ valence electrons}$$

$$\text{four } \mathbf{H} \text{ atoms } = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{total of 12 valence electrons in the molecule}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

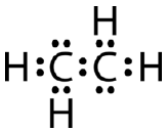


Figure 12.4.1: Incorrect dot structure of ethene. (CK12 License)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having to share two pairs instead of only one pair.

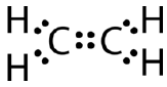


Figure 12.4.2: Correct dot structure for ethene. (CK12 License)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as shown in the figure below.

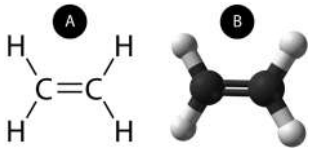


Figure 12.4.3: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

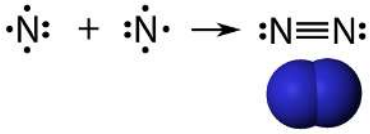


Figure 12.4.4: Triple bond in N_2.

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.

Summary

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

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12.5: Writing Lewis Structures for Covalent Compounds

Learning Objectives

- Draw Lewis structures for covalent compounds.

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

How-to: Constructing Lewis electron structures

1. Determine the total number of valence electrons in the molecule or ion.

- Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.)
- If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion.

  For CO_3^{2-}, for example, we add two electrons to the total because of the -2 charge.

2. Arrange the atoms to show specific connections.

- When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure.
- Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.

- In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

- These electrons will usually be lone pairs.

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

- We will explain later that some atoms are able to accommodate more than eight electrons.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.

- This will not change the number of electrons on the terminal atoms.

7. Final check

- Always make sure all valence electrons are accounted for and that each atom has an octet of electrons, except for hydrogen (with two electrons).
- The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

Example 12.5.1: Water

Write the Lewis Structure for H_2O.

Solution

Solutions to Example 10.4.1

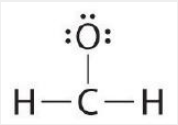
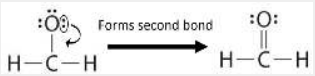
Steps for Writing Lewis Structures	Example **12.5.1**
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
2. Arrange the atoms to show specific connections.	H O H Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Placing one bonding pair of electrons between the O atom and each H atom gives H -O- H with 4 electrons left over. Each H atom has a full valence shell of 2 electrons.
5. If any electrons are left over, place them on the central atom.	Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure: 
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	Not necessary.
7. Final check.	The Lewis structure gives oxygen an octet and each hydrogen 2 electrons.

Example 12.5.2

Write the Lewis structure for the CH_2O molecule

Solution

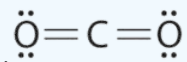
Solutions to Example 10.4.2

Steps for Writing Lewis Structures	Example **12.5.2**
1. Determine the total number of valence electrons in the molecule or ion.	Each hydrogen atom (group 1) has 1 valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.
2. Arrange the atoms to show specific connections.	 Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.	Placing a bonding pair of electrons between each pair of bonded atoms gives the following:  6 electrons are used, and 6 are left over.
4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:  Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.
5. If any electrons are left over, place them on the central atom.	Not necessary. There are no electrons left to place on the central atom.
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond: 
7. Final check	Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

? Exercise 12.5.1

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

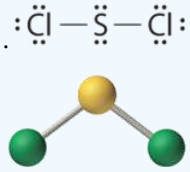
Answer CO_2





Carbon dioxide

Answer SCl_2



The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Writing Lewis Structures for Polyatomic Ions (CK-12)

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, $\mathbf{NH_4^+}$, is formed when a hydrogen ion ($\mathbf{H^+}$) attaches to the lone pair of an ammonia ($\mathbf{NH_3}$) molecule in a coordinate covalent bond.

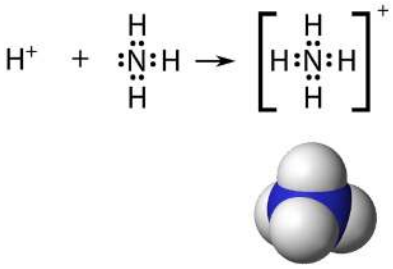


Figure **12.5.3**: The ammonium ion. (CK12 License)

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$\mathbf{1\ N}\text{ atom } = \mathbf{5}\text{ valence electrons}$$

$$\mathbf{4\ H}\text{ atoms } = \mathbf{4 \times 1 = 4}\text{ valence electrons}$$

subtract 1 electron for the $\mathbf{1+}$ charge of the ion

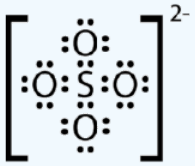
total of 8 valence electrons in the ion

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside of the brackets.

Exercise 12.5.2

Draw the Lewis electron dot structure for the sulfate ion.

Answer (CK12 License)



Exceptions to the Octet Rule (BC Campus)

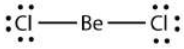
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

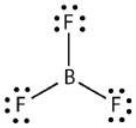


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

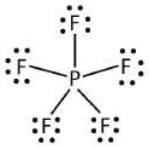
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting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



Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:



Formally, the P atom has 10 electrons in its valence shell.

Example 12.5.3: Octet Violations

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

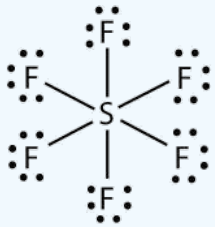
a. ClO
b. SF_6

Solution

a. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



b. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:



? Exercise 12.5.3: Xenon Difluoride

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

Answer



The Xe atom has an expanded valence shell with more than eight electrons around it.

Summary

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds. There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

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12.6: Violations of the Octet Rule

Learning Objective

- Recognize the three major types of violations of the octet rule.

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

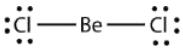
There are three violations to the octet rule. **Odd-electron molecules** are the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are **NO**, $\mathbf{NO_2}$, and $\mathbf{ClO_2}$. The Lewis electron dot diagram for **NO** is as follows:



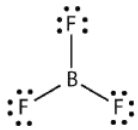
Nitrogen and oxygen share four electrons between them. Oxygen has two lone pairs while nitrogen has one full lone pair and one additional electron.

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

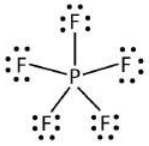
Electron-deficient molecules are the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only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



Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the **B** atom. A well-known example is $\mathbf{BF_3}$:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called **expanded valence shell molecules**. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is $\mathbf{PF_5}$. The only reasonable Lewis electron dot diagram for this compound has the **P** atom making five covalent bonds:



Formally, the **P** atom has 10 electrons in its valence shell.

Example 12.6.1

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

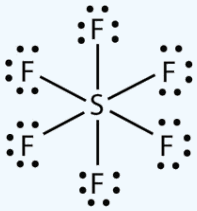
a. **ClO**
b. $\mathbf{SF_6}$

Solution

1. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



2. In $\mathbf{SF_6}$, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:

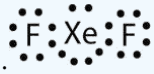


? Exercise 12.6.1: Xenon Difluoride

Identify the violation to the octet rule in $\mathbf{XeF_2}$ by drawing a Lewis electron dot diagram.

Answer

The Xe atom has an expanded valence shell with more than eight electrons around it.



Summary

There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

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12.7: Resonance - Equivalent Lewis Structures for the Same Molecule

Learning Objectives

- Explain the concept of resonance and how it works with within molecules.

Resonance

There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone (O_3) molecule in Figure **12.7.1**. There are a total of 18 electrons in the structure and so the following two structures are possible.

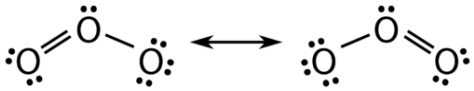


Figure **12.7.1**: Resonance forms of ozone. Note the use of the double-headed arrow.

The structure on the left (**12.7.1**) can be converted to the structure on the right by a shifting of electrons without altering the positions of the atoms.

It was once thought that the structure of a molecule such as O_3 consisted of one single bond and one double bond which then shifted back and forth as shown above. However, further studies showed that the two bonds are identical. Any double covalent bond between two given atoms is typically shorter than a single covalent bond. Studies of the O_3 and other similar molecules showed that the bonds were identical in length. Interestingly, the length of the bond is in between the lengths expected for an O–O single bond and a double bond.

Resonance is the use of two or more Lewis structures to represent the covalent bonding in a molecule. One of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule which displays resonance is that of an average or a hybrid of all the resonance structures. In the case of the O_3 molecule, each of the covalent bonds between O atoms are best thought of as being "one and a half" bonds, as opposed to either a pure single bond or a pure double bond. This "half-bond" can be shown as a dotted line in both the Lewis structure and the molecular model (Figure **12.7.2**).

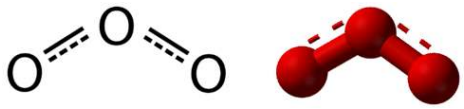


Figure **12.7.2**: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure **12.7.1**.

Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion, NO_3^- in Figure **12.7.3**.

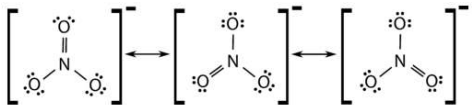


Figure **12.7.3**: Resonance structure of nitrate anion.

The bond lengths between the central N atom and each O atom are identical and the bonds can be approximated as being equal to one and one-third bonds.

Summary

- Resonance structures are averages of different Lewis structure possibilities.
- Bond lengths are intermediate between covalent bonds and covalent double bonds.

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12.8: Predicting the Shapes of Molecules

Learning Objective

- Determine the shape of simple molecules.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:



Figure **12.8.1**: Beryllium hydride and carbon dioxide bonding.

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

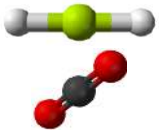


Figure **12.8.2**: Beryllium hydride and carbon dioxide models. (CK12 Licence)

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:

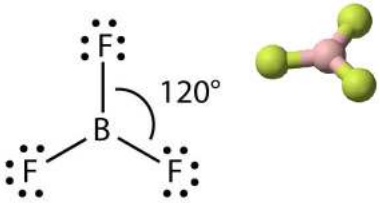


Figure **12.8.3**: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

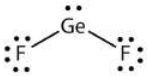


Figure **12.8.4**: Germanium difluoride bonding.

From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 12.8.1 Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

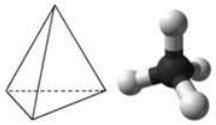


Figure 12.8.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

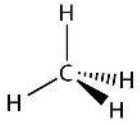


Figure 12.8.6: Methane bonding. (CK12 Licence)

NH_3 is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

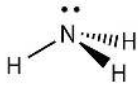


Figure 12.8.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.



Figure 12.8.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 12.8.9.



Figure 12.8.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.

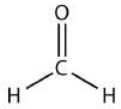


Figure 12.8.10: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Table **12.8.1** summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table **12.8.1**: Summary of Molecular Shapes

Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Geometry	Molecular Shape
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent

Example 12.8.1

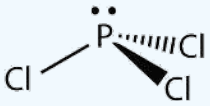
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

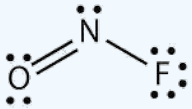
The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Exercise 12.8.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

? Exercise 12.8.2

Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

Answer

Trigonal planar about both central C atoms.

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

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12.9: Electronegativity and Polarity - Why Oil and Water Don't Mix

Learning Objectives

- Explain how polar compounds differ from nonpolar compounds.
- Determine if a molecule is polar or nonpolar.
- Given a pair of compounds, predict which would have a higher melting or boiling point.

Bond Polarity

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

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure **12.9.1**.

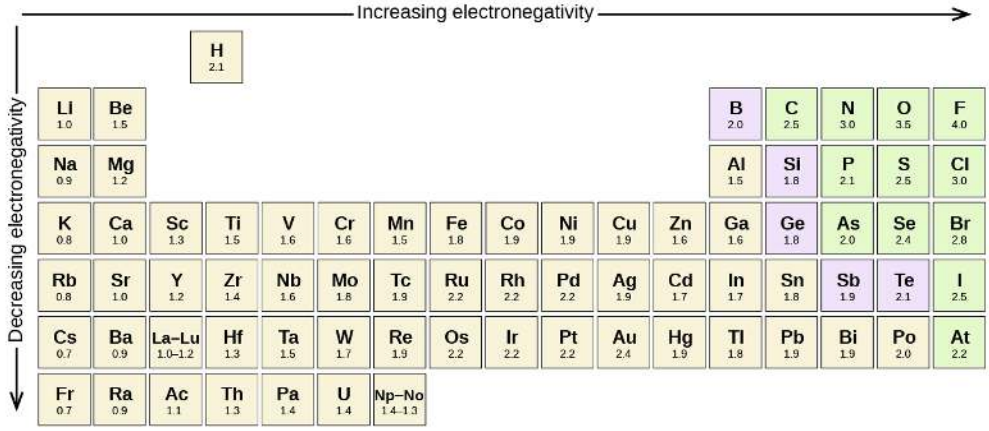


Figure **12.9.1**: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

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

difference of the electronegativities of the two atoms involved in the covalent bond

Electronegativity Difference	Bond Type
0–0.4	pure covalent
0.5–2.0	polar covalent
>2.0	likely ionic

Nonpolar Covalent Bonds

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

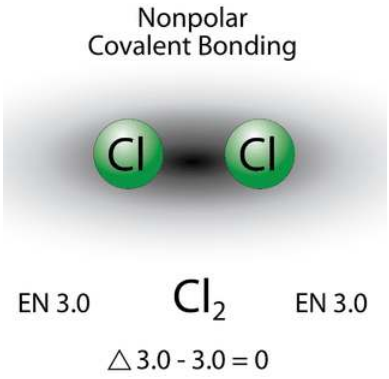


Figure **12.9.2**: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

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

Polar Covalent Bonds

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

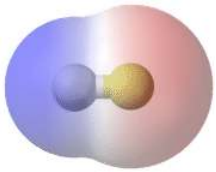


Figure **12.9.3**: In the polar covalent bond of **HF**, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

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

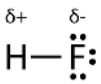


Figure **12.9.4**: Use of δ to indicate partial charge.

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



Figure **12.9.5**: Use of crossed arrow to indicate polarity.



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

Example 12.9.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure **12.9.1**, we can calculate the difference of the electronegativities of the atoms involved in the bond.

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

Exercise 12.9.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

Molecular Polarity

To determine if a molecule is polar or nonpolar, it is generally useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical—bonded to the same element with no unshared pairs of electrons. **Polar molecules** are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well, as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming that you do, you can look at the structure of each one and decide if it is polar or not, *whether or not you know the individual atom's electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as **HF**, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.



Figure 12.9.6: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the **C** atom to each **O** atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the **H** atoms toward the **O** atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

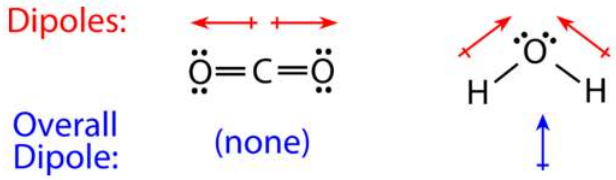


Figure 12.9.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral **H** atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

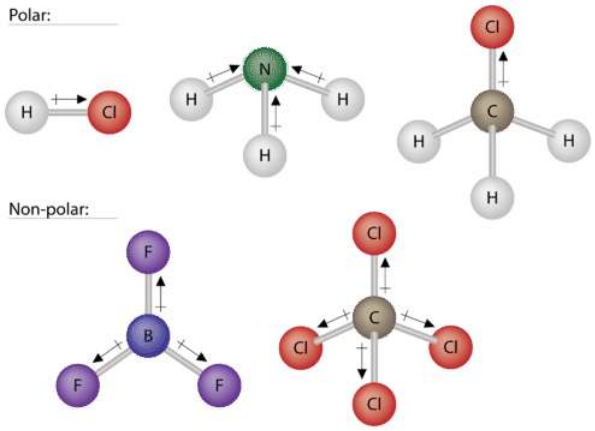


Figure 12.9.8: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment do not cancel.

Steps to Identify Polar Molecules

1. Draw the Lewis structure.
2. Figure out the geometry (using VSEPR theory).
3. Visualize or draw the geometry.
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it).
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure **12.9.14**). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

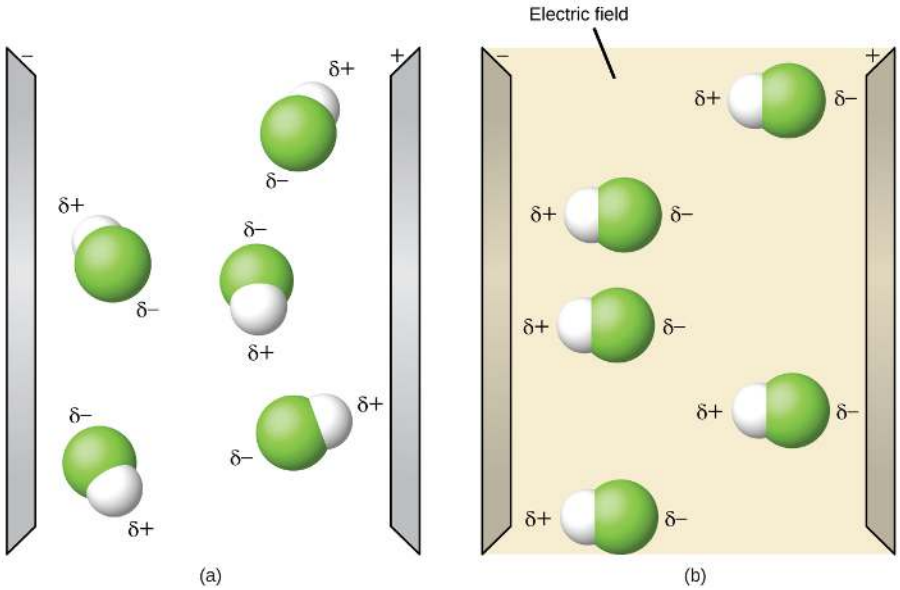


Figure **12.9.9**: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

Example 12.9.2:

Label each of the following as polar or nonpolar.

a. Water, H_2O:

b. Methanol, CH_3OH:

c. Hydrogen Cyanide, HCN: H–C≡N

d. Oxygen, O_2:

e. Propane, C_3H_8: 

Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-OH$ side is different from the other 3 $-H$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

? Exercise 12.9.2

Label each of the following as polar or nonpolar.

a. SO_3
b. NH_3

Answer a

nonpolar

Answer b

polar

Contributions & Attributions

- StackExchange (thomij).

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CHAPTER OVERVIEW

13: Gases

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Of the three basic phases of matter—solids, liquids, and gases—only one of them has predictable physical properties: gases. In fact, the study of the properties of gases was the beginning of the development of modern chemistry from its alchemical roots. The interesting thing about some of these properties is that they are independent of the identity of the gas. That is, it doesn't matter if the gas is helium gas, oxygen gas, or sulfur vapors; some of their behavior is predictable and very similar. In this chapter, we will review some of the common behaviors of gases. Gases have no definite shape or volume; they tend to fill whatever container they are in. They can compress and expand, sometimes to a great extent. Gases have extremely low densities, a one-thousandth or less of the density of a liquid or solid. Combinations of gases tend to mix together spontaneously—that is, they form solutions. Air, for example, is a solution of mostly nitrogen and oxygen. Any understanding of the properties of gases must be able to explain these characteristics.

13.1: Extra-Long Straws
13.2: Kinetic Molecular Theory- A Model for Gases
13.3: Pressure - The Result of Constant Molecular Collisions
13.4: The Combined Gas Law- Pressure, Volume, and Temperature
13.5: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles
13.6: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen
13.7: Boyle's Law - Pressure and Volume
13.8: Charles's Law- Volume and Temperature
13.9: Gay-Lussac's Law- Temperature and Pressure
13.10: Avogadro's Law- Volume and Moles
13.11: Carbon Dioxide and Climate Change

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13.1: Extra-Long Straws

A drinking straw is a tube for transferring a beverage from its container to the mouth of the drinker and is typically a thin tube of plastic (such as polypropylene and polystyrene) or other material. Many people believe that when they drink a liquid they are sucking the liquid up, however the liquid is really being pushed up. A straw works because when you suck the air out of the straw, it creates a vacuum. This causes a decrease in air pressure on the inside of the straw. Since the atmospheric pressure is greater on the outside of the straw, liquid is forced into and up the straw and into your mouth (Figure **13.1.1**).

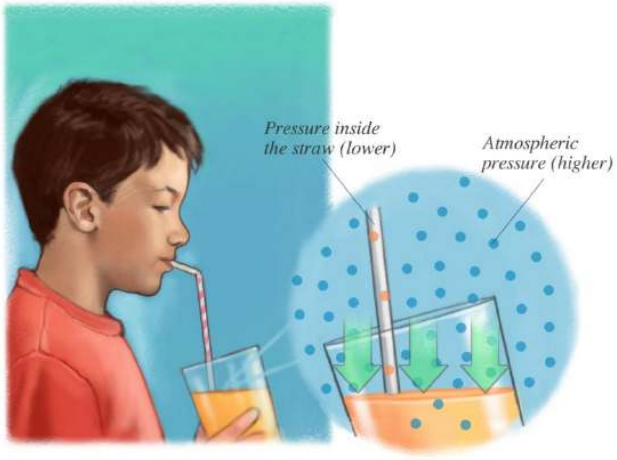


Figure **13.1.1**: As you suck the air out of the straw, it creates a low pressure zone inside of it. With a low pressure zone, there is nothing pushing down on the juice, so it moves upward easily. (CC BY-NC 4.0; Ümit Kaya)

How Long of a Straw is Possible?

With the straw just sitting in the glass, the pressure on the surface of the tea is the same all over, including on the little bit of surface inside the straw. When you suck the air out of the straw, you decrease the pressure inside the straw, allowing the higher pressure on the rest of the surface to push the tea up the straw and into your mouth. Because it is really the atmosphere that is doing the pushing, the atmospheric pressure limits how high water will go up a straw.

If you formed a perfect vacuum within the straw, the pressure outside of the straw at sea level would be enough to push water to a total height of about 10.3 m. A 10.3-m column of water exerts the same pressure—101,325 N/m^2 or 14.7 lb/in^2 (psi)—as do the gas molecules in our atmosphere. At sea level, the air pressure is enough to support a column of water about thirty feet high. This means that even if you could suck all the air out of a forty-foot straw, the water would not rise more than thirty feet.

Contributions & Attributions

- Lisa Peck's Conceptual Physics Class

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13.2: Kinetic Molecular Theory- A Model for 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**. It is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic; that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure **13.2.1** shows a representation of how we mentally picture the gas phase.

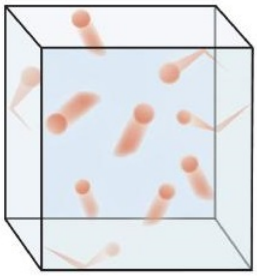


Figure **13.2.1**: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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 so well that the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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13.3: Pressure - The Result of Constant Molecular Collisions

Learning Objectives

- Define *pressure*.
- Learn the units of pressure and how to convert between them.

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. The accumulation of all these forces distributed over the area of the walls of the container causes something we call pressure. **Pressure** (***P***) is defined as the force of all the gas particle/wall collisions divided by the area of the wall:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

All gases exert pressure; it is one of the fundamental measurable quantities of this phase of matter. Even our atmosphere exerts pressure—in this case, the gas is being "held in" by the earth's gravity, rather than the gas being in a container. The pressure of the atmosphere is about 14.7 pounds of force for every square inch of surface area: 14.7 lb/in^2.

Pressure has a variety of units. The formal, SI-approved unit of pressure is the *pascal* (Pa), which is defined as 1 N/m^2 (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the **atmosphere** (atm), which was originally defined as the average atmospheric pressure at sea level.

However, "average atmospheric pressure at sea level" is difficult to pinpoint because of atmospheric pressure variations. A more reliable and common unit is **millimeters of mercury** (mmHg), which is the amount of pressure exerted by a column of mercury exactly 1 mm high. An equivalent unit is the **torr**, which equals 1 mmHg. (The torr is named after Evangelista Torricelli, a seventeenth-century Italian scientist who invented the mercury barometer.) With these definitions of pressure, the atmosphere unit is redefined: 1 atm is defined as exactly 760 mmHg, or 760 torr. We thus have the following equivalents:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

We can use these equivalents as with any equivalence—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

Example 13.3.1: Pressure Conversion

How many atmospheres are there in 595 torr?

Solution

Solutions to Example 11.3.1

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 595 torr Find: ? atm
List other known quantities.	1 atm = 760 torr
Prepare a concept map.	torr → atm $\frac{1\ atm}{760\ torr}$
Cancel units and calculate.	$595\ \cancel{torr} \times \frac{1\ atm}{760\ \cancel{torr}} = 0.783\ atm$
Think about your result.	595 torr is less than 760 torr so the final answer should be less than 1 atm.

Exercise 13.3.1

How many atmospheres are there in 1,022 torr?

Answer

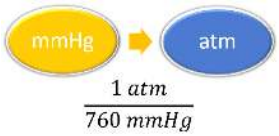
1.345 atm

Example 13.3.2: Mars

The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

Solution

Solutions to Example 11.3.2

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 6.01mmHg Find: ? atm
List other known quantities.	1 atm = 760 mmHg
Prepare a concept map.	 $\frac{1\ atm}{760\ mmHg}$
Cancel units and calculate.	$6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$
Think about your result.	6.01 is a very small number relative to 760 mmHg, just like the value in atmospheres.

Exercise 13.3.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

Answer

652 torr

Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

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13.4: The Combined Gas Law- Pressure, Volume, and Temperature

Learning Objectives

- Learn and apply the Combined Gas Law.

One thing we notice about all the gas laws is that, collectively, volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **Combined Gas Law**, and its mathematical form is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \; at \; constant \; n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in Kelvin.

Example 13.4.1:

A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?

Solution

Solutions to Example 11.4.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: V_1 = 8.33 L, P_1 = 1.82 atm, and T_1 = 286 K V2 = 5.72 L and T_2 = 355 K Find: $P2$ = ? atm
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $P_2 = \frac{P_1V_1T_2}{T_1V_2}$
Calculate.	Now substitute the known quantities into the equation and solve. $P_2 = \frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})} = 3.22atm$
Think about your result.	Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

Exercise 13.4.1

If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?

Answer

105 mL

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

Summary

- The Combined Gas Law relates pressure, volume, and temperature of a gas.

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13.5: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles

Learning Objectives

- Explain the Ideal Gas Law.

There are a number of chemical reactions that require ammonia. In order to carry out the reaction efficiently, we need to know how much ammonia we have for stoichiometric purposes. Using gas laws, we can determine the number of moles present in the tank if we know the volume, temperature, and pressure of the system.

Ideal Gas Law

The Combined Gas Law shows that the pressure of a gas is inversely proportional to volume and directly proportional to temperature. Avogadro's Law shows that volume or pressure is directly proportional to the number of moles of gas. Putting these together leaves us with the following equation:

$$\frac{P_1 \times V_1}{T_1 \times n_1} = \frac{P_2 \times V_2}{T_2 \times n_2}$$

As with the other gas laws, we can also say that $\frac{(P \times V)}{(T \times n)}$ is equal to a constant. The constant can be evaluated provided that the gas being described is considered to be ideal.

The **Ideal Gas Law** is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas. If we substitute in the variable R for the constant, the equation becomes:

$$\frac{P \times V}{T \times n} = R$$

The Ideal Gas Law is conveniently rearranged to look this way, with the multiplication signs omitted:

$$PV = nRT$$

The variable R in the equation is called the **ideal gas constant**.

Evaluating the Ideal Gas Constant

The value of R, the ideal gas constant, depends on the units chosen for pressure, temperature, and volume in the ideal gas equation. It is necessary to use Kelvin for the temperature and it is conventional to use the SI unit of liters for the volume. However, pressure is commonly measured in one of three units: $\mathbf{kPa}$, $\mathbf{atm}$, or $\mathbf{mm\,Hg}$. Therefore, R can have three different values.

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

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

This is the value of R that is to be used in the ideal gas equation when the pressure is given in $\mathbf{kPa}$. The table below shows a summary of this and the other possible values of R. It is important to choose the correct value of R to use for a given problem.

Table 13.5.1: Values of the Ideal Gas Constant

Unit of P	Unit of V	Unit of n	Unit of T	Value and Unit of R
kPa	L	mol	K	$8.314\ \text{J/K} \cdot \text{mol}$
atm	L	mol	K	$0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol}$
mm Hg	L	mol	K	$62.36\ \text{L} \cdot \text{mm Hg/K} \cdot \text{mol}$

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

Example 13.5.1 Oxygen Gas

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

Solution

Solutions to Example 11.5.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: • $P = 88.4\ \text{kPa}$ • $T = 19°\text{C} = 292\ \text{K}$ Mass $\text{O}_2 = 3.76\ \text{g}$ Find: V = ? L
List other known quantities.	$\text{O}_2 = 32.00\ \text{g/mol}$ $R = 8.314\ \text{J/K} \cdot \text{mol}$
Plan the problem.	1. First, determine the number of moles of O_2 from the given mass and the molar mass. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate.	1. $$3.76\ \cancel{g} \times \frac{1\ \text{mol O}_2}{32.00\ \cancel{g}\ \text{O}_2} = 0.1175\ \text{mol O}_2$$ 2. Now substitute the known quantities into the equation and solve. $$V = \frac{nRT}{P}$$ $$= \frac{0.1175\ \cancel{\text{mol}} \times 8.314\ \cancel{\text{J/K}} \cdot \cancel{\text{mol}} \times 292\ \cancel{\text{K}}}{88.4\ \cancel{\text{kPa}}}$$ $$= 3.23\ \text{L O}_2$$
Think about your result.	The number of moles of oxygen is far less than one mole, so the volume should be fairly small compared to molar volume (22.4 L/mol) since the pressure and temperature are reasonably close to standard. The result has three significant figures because of the values for T and P. Since a joule $(\text{J}) = \text{kPa} \cdot \text{L}$, the units cancel out correctly, leaving a volume in liters.

Example 13.5.2: Argon Gas

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

Solutions to Example 11.5.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: n = 4.22 mol P = 1.21 atm T = 34°C Find: V = ? L
List other known quantities.	none
Plan the problem.	1. The first step is to convert temperature to Kelvin. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate.	1. 34 + 273 = 307 K 2. Now substitute the known quantities into the equation and solve. $$V = \frac{(4.22\ \cancel{mol})(0.08205\frac{L.\cancel{atm}}{\cancel{mol.K}})(307\ \cancel{K})}{1.21\ \cancel{atm}}$$ $$= 87.9\ L$$
Think about your result.	The number of moles of Ar is large so the expected volume should also be large.

Exercise 13.5.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

Exercise 13.5.2

For a 0.00554 mol sample of H_2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

Summary

- The Ideal Gas Law is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas.

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13.6: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen

Learning Objectives

- Explain Dalton's Law of Partial Pressures.

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are 96.5% carbon dioxide and 3% nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus would contribute a pressure well over $2700\ \text{mm Hg}$. And there is no oxygen present, so we couldn't breathe there. Not that we would want to go to Venus, as the surface temperature is usually over 460°C.

Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about 78% nitrogen and 21% oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up 78% of the gas particles in a given sample of air, it exerts 78% of the pressure. If the overall atmospheric pressure is $1.00\ \text{atm}$, then the pressure of just the nitrogen in the air is $0.78\ \text{atm}$. The pressure of the oxygen in the air is $0.21\ \text{atm}$.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of nitrogen is represented by P_{N_2}. **Dalton's Law of Partial Pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's Law can be expressed with the following equation:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$$

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, P_1 and P_2, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If $P_1 = 300\ \text{mm Hg}$ and $P_2 = 500\ \text{mm Hg}$, then $P_{\text{total}} = 800\ \text{mm Hg}$.

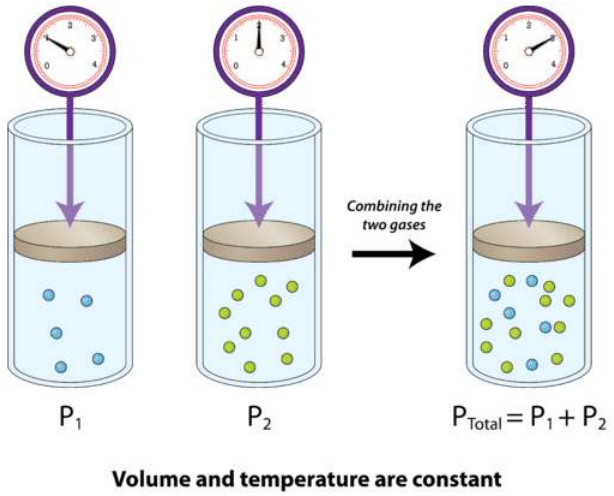


Figure **13.6.1**: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

Collecting Gases Over Water

You need to do a lab experiment where hydrogen gas is generated. In order to calculate the yield of gas, you have to know the pressure inside the tube where the gas is collected. But how can you get a barometer in there? Very simple: you don't. All you need

is the atmospheric pressure in the room. As the gas pushes out the water, it is pushing against the atmosphere, so the pressure inside is equal to the pressure outside.

Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (Figure **13.6.2**). A bottle is filled with water and placed upside-down in a pan of water. The reaction flask is fitted with rubber tubing, which is then fed under the bottle of water. As the gas is produced in the reaction flask, it exits through the rubber tubing and displaces the water in the bottle. When the bottle is full of the gas, it can be sealed with a lid.



Figure **13.6.2**: A gas produced in a chemical reaction can be collected by water displacement.

Because the gas is collected over water, it is not pure, but is mixed with vapor from the evaporation of the water. Dalton's Law can be used to calculate the amount of the desired gas by subtracting the contribution of the water vapor.

$$P_{\text{Total}} = P_g + P_{H_2O}$$

where P_g is the pressure of the desired gas, which can be solved for:

$$P_g = P_{Total} - P_{H_2O}$$

In order to solve a problem, it is necessary to know the vapor pressure of water at the temperature of the reaction (see table below). The sample problem illustrates the use of Dalton's Law when a gas is collected over water.

Table **13.6.1**: Vapor Pressure of Water (**mm Hg**) at Selected Temperatures (**°C**)

0	5	10	15	20	25	30	35	40	45	50	55	60
4.58	6.54	9.21	12.79	17.54	23.76	31.82	42.18	55.32	71.88	92.51	118.04	149.38

Example 14.14.1

A certain experiment generates **2.58 L** of hydrogen gas, which is collected over water. The temperature is **20°C** and the atmospheric pressure is **98.60 kPa**. Find the volume that the dry hydrogen would occupy at STP.

Solution

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

Known

- $V_{\text{Total}} = 2.58\ \text{L}$
- $T = 20°\text{C} = 293\ \text{K}$
- $P_{\text{Total}} = 98.60\ \text{kPa} = 739.7\ \text{mm Hg}$

Unknown

- V_{H_2} at STP $=?\ \text{L}$

The atmospheric pressure is converted from **kPa** to **mm Hg** in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

Step 2: Solve.

$$\begin{aligned} P_{H_2} &= P_{\text{Total}} - P_{H_2O} \\ &= 739,7 \text{ mm Hg} - 17.54 \text{ mm Hg} \\ &= 722.2 \text{ mm Hg} \end{aligned}$$

Now the combined gas law is used, solving for V_2, the volume of hydrogen at STP.

$$\begin{aligned} V_2 &= \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1} \\ &= \frac{722.2 \text{ mm Hg} \times 2.58 \text{ L} \times 273 \text{ K}}{760 \text{ mm Hg} \times 293 \text{ K}} \\ &= 2.28 \text{ L } H_2 \end{aligned}$$

Step 3: Think about your result.

If the hydrogen gas were to be collected at STP and without the presence of the water vapor, its volume would be **2.28 L**. This is less than the actual collected volume because some of that is water vapor. The conversion using STP is useful for stoichiometry purposes.

Summary

- Dalton's Law of Partial Pressures states that the total pressure in a system is equal to the sum of the partial pressures of the gases present.
- The vapor pressure due to water in a sample can be corrected for, in order to get the true value for the pressure of the gas.

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13.7: Boyle’s Law - Pressure and Volume

Learning Objectives

- Learn what is meant by the term *gas laws*.
- Learn and apply Boyle’s Law.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (P) and volume (V), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [n]), if the temperature (T) of the gas was kept constant, pressure and volume were related: as one increases, the other decreases. As one decreases, the other increases. This means that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{ constant at constant n and T}$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled P_1 and V_1 and the new conditions are labeled P_2 and V_2, we have

$$P_1V_1 = \text{constant} = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant n and T}$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's Law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure 13.7.1 shows two representations of how Boyle’s Law works.

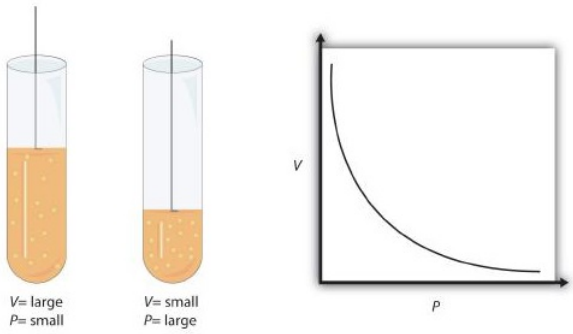


Figure 13.7.1: Boyle’s Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle’s Law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle’s Law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won’t matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

Example 13.7.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

Solutions to Example 11.8.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: P_1 = 2.44 atm and V_1 = 4.01 L P_2 = 1.93 atm Find: V_2 = ? L
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{P_1 \times V_1}{P_2}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.44 \cancel{\text{ atm}} \times 4.01 \text{ L}}{1.93 \cancel{\text{ atm}}} = 5.07 \text{ L}$$
Think about your result.	We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's Law.

Exercise 13.7.1

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

Answer

124 mL

As mentioned, you can use any units for pressure and volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

Example 13.7.2:

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

Solutions to Example 11.8.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: P_1 = 722 torr and V_1 = 88.8 mL V_2 = 0.633 L Find: P_2 = ? torr
List other known quantities.	1 L = 1000 mL to have the same units for volume.
Plan the problem.	1. Perform the conversion of the second volume unit from L to mL. 2. Rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times V_1}{V_2}$$
Cancel units and calculate.	1. $$0.663 \cancel{L} \times \frac{1000\,ml}{1\,\cancel{L}} = 663\,ml$$ 2. Substitute the known quantities into the equation and solve. $$P_2 = \frac{722\ \text{torr} \times 88.8\ \cancel{\text{mL}}}{663\ \cancel{\text{mL}}} = 96.7\ \text{torr}$$
Think about your result.	When the volume increased, the pressure decreased, which is as expected for Boyle's Law.

? Exercise 13.7.2

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

Answer

119 mL

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's Law relates the pressure and volume of a gas at constant temperature and amount.

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13.8: Charles's Law- Volume and Temperature

Learning Objectives

- Learn and apply Charles's Law.

Everybody enjoys the smell and taste of freshly-baked bread. It is light and fluffy as a result of the action of yeast on sugar. The yeast converts the sugar to carbon dioxide, which at high temperatures causes the dough to expand. The end result is an enjoyable treat, especially when covered with melted butter.

Charles's Law

French physicist Jacques Charles (1746-1823) studied the effect of temperature on the volume of a gas at constant pressure. **Charles's Law** states that the volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant. The absolute temperature is temperature measured with the Kelvin scale. The Kelvin scale must be used because zero on the Kelvin scale corresponds to a complete stop of molecular motion.

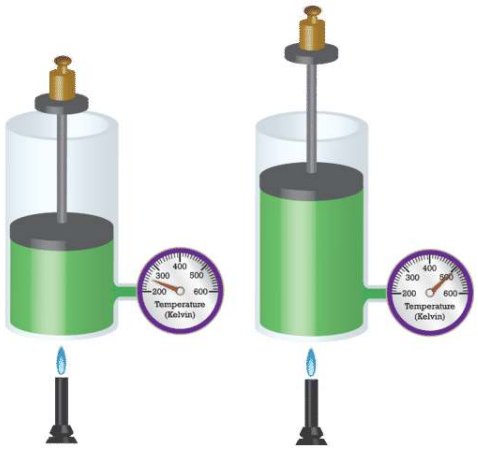


Figure **13.8.1**: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

Mathematically, the direct relationship of Charles's Law can be represented by the following equation:

$$\frac{V}{T} = k$$

As with Boyle's Law, k is constant only for a given gas sample. The table below shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

Table **13.8.1**: Temperature-Volume Data

Temperature (K)	Volume (mL)	$\frac{V}{T} = k \left(\frac{\text{mL}}{\text{K}}\right)$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in the figure below.

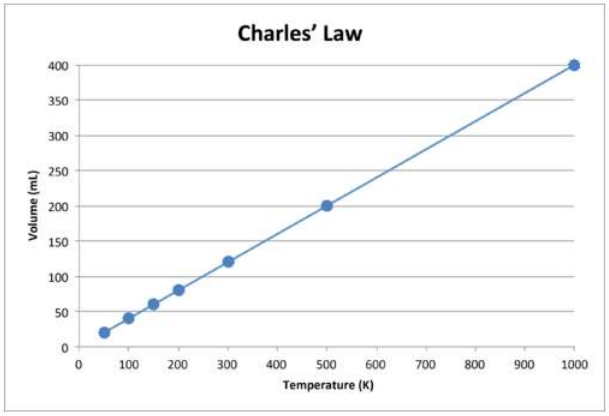


Figure 13.8.2:The volume of a gas increases as the Kelvin temperature increases.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero. The temperature at which this change into the liquid state occurs varies for different gases.

Charles's Law can also be used to compare changing conditions for a gas. Now we use V_1 and T_1 to stand for the initial volume and temperature of a gas, while V_2 and T_2 stand for the final volume and temperature. The mathematical relationship of Charles's Law becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that $\mathrm{K} = {}^\circ\mathrm{C} + 273$.

Example 13.8.1:

A balloon is filled to a volume of $2.20\ \mathrm{L}$ at a temperature of $22^\circ\mathrm{C}$. The balloon is then heated to a temperature of $71^\circ\mathrm{C}$. Find the new volume of the balloon.

Solution

Solutions to Example 11.5.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $V_1 = 2.20\ \text{L}$ and $T_1 = 22°\text{C} = 295\ \text{K}$ $T_2 = 71°\text{C} = 344\ \text{K}$ Find: V_2 = ? L
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{V_1 \times T_2}{T_1}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.20\ \text{L} \times 344\ \cancel{\text{K}}}{295\ \cancel{\text{K}}} = 2.57\ \text{L}$$
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

? Exercise 13.8.1

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

Answer

1.82 L

✔ Example 13.8.2:

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must be the temperature of the gas for its volume to be 25.0 L?

Solution

Solutions to Example 11.5.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Given:T_1 = -27°C and V_1 = 34.8 L V_2 = 25.0 L Find: T_2 = ? K
List other known quantities.	K = -27°C + 273
Plan the problem.	1. Convert the initial temperature to Kelvin 2. Rearrange the equation algebraically to solve for T_2. $$T_2 = \frac{V_2 \times T_1}{V_1}$$
Cancel units and calculate.	1. −67°C + 273 = 206 K 2. Substitute the known quantities into the equation and solve. $$T_2 = \frac{25.0 \cancel{L} \times 206\ \text{K}}{34.8 \cancel{L}} = 148\ \text{K}$$
Think about your result.	This is also equal to −125°C. As temperature decreases, volume decreases—which it does in this example.

? Exercise 13.8.2

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

Answer

235 K, or −38°C

Summary

- Charles's Law relates the volume and temperature of a gas at constant pressure and amount.

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13.9: Gay-Lussac's Law- Temperature and Pressure

Learning Objectives

- Explain Gay-Lussac's Law.

Propane tanks are widely used with barbeque grills. But it's not fun to find out halfway through grilling that you have run out of gas. You can buy gauges that measure the pressure inside the tank to see how much is left. The gauge measures pressure and will register a higher pressure on a hot day than it will on a cold day. So you need to take the air temperature into account when you decide whether or not to refill the tank before your next cook-out.

Gay-Lussac's Law

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's Law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's Law is very similar to Charles's Law, with the only difference being the type of container. Whereas the container in a Charles's Law experiment is flexible, it is rigid in a Gay-Lussac's Law experiment.



Figure **13.9.1**: Joseph Gay-Lussac.

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume, its pressure continually decreases until the gas condenses to a liquid.

Example 13.9.1

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

Solution

Solutions to Example 11.10.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $P_1 = 3.00\ \text{atm}$ $T_1 = 25°\text{C} = 298\ \text{K}$ $T_2 = 845°\text{C} = 1118\ \text{K}$ Find: $P_2 = ?\ \text{atm}$
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times T_2}{T_1}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$P_2 = \frac{3.00\ \text{atm} \times 1118\ \cancel{\text{K}}}{298\ \cancel{\text{K}}} = 11.3\ \text{atm}$$
Think about your result.	The pressure increases dramatically due to a large increase in temperature.

Summary

- Pressure and temperature at constant volume are directly proportional.

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13.10: Avogadro's Law- Volume and Moles

A flat tire is not very useful. It does not cushion the rim of the wheel and creates a very uncomfortable ride. When air is added to the tire, the pressure increases as more molecules of gas are forced into the rigid tire. How much air should be put into a tire depends on the pressure rating for that tire. Too little pressure and the tire will not hold its shape. Too much pressure and the tire could burst.

Avogadro's Law

You have learned about Avogadro's hypothesis: equal volumes of any gas at the same temperature and pressure contain the same number of molecules. It follows that the volume of a gas is directly proportional to the number of moles of gas present in the sample. **Avogadro's Law** states that the volume of a gas is directly proportional to the number of moles (or number of particles) of gas when the temperature and pressure are held constant. The mathematical expression of Avogadro's Law is:

$$V = k \times n$$

or

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

where n is the number of moles of gas and k is a constant. Avogadro's Law is in evidence whenever you blow up a balloon. The volume of the balloon increases as you add moles of gas to the balloon by blowing it up.

If the container holding the gas is rigid rather than flexible, pressure can be substituted for volume in Avogadro's Law. Adding gas to a rigid container makes the pressure increase.

Example 13.10.1

A balloon has been filled to a volume of $1.90\ \text{L}$ with $0.0920\ \text{mol}$ of helium gas. If $0.0210\ \text{mol}$ of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

Solution

Solutions to Example 11.11.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $V_1 = 1.90\ \text{L}$ $n_1 = 0.0920\ \text{mol}$ Find: $V_2 = ?\ \text{L}$
List other known quantities.	Note that the final number of moles has to be calculated by adding the original number of moles to the moles of added helium. $n_2 = 0.0920 + 0.0210 = 0.1130\ \text{mol}$
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $V_2 = \frac{V_1 \times n_2}{n_1}$
Calculate.	Now substitute the known quantities into the equation and solve. $V_2 = \frac{1.90\ \text{L} \times 0.1130\ \cancel{\text{mol}}}{0.0920\ \cancel{\text{mol}}} = 2.33\ \text{L}$
Think about your result.	Since a relatively small amount of additional helium was added to the balloon, its volume increases slightly.

Exercise 13.10.1

A 12.8 L volume of gas contains .000498 moles of oxygen gas. At constant temperature and pressure, what volume does .0000136 moles of the gas fill?

Answer

0.350 L

Summary

- Calculations for relationships between volume and number of moles of a gas can be performed using Avogadro's Law.

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13.11: Carbon Dioxide and Climate Change

Learning Objectives

- Define global warming, climate change, the greenhouse effect, and greenhouse gases.
- Discuss strategies for reducing the intensity of the human influence on the greenhouse effect.

Global warming refers to the increase in the average temperature of the Earth's atmosphere due to elevated greenhouse gas concentrations, heightening the greenhouse effect. **Climate change** includes both global warming driven by human-induced emissions of greenhouse gases and the resulting large-scale shifts in weather patterns. Though there have been previous periods of climatic change, since the mid-20th century humans have had an unprecedented impact on Earth's climate system and caused change on a global scale.

The largest driver of warming is the emission of gases that create a greenhouse effect, of which more than 90% are carbon dioxide (CO_2) and methane. Fossil fuel burning (coal, oil, and natural gas) for energy consumption is the main source of these emissions, with additional contributions from agriculture, deforestation, and manufacturing. The human cause of climate change is not disputed by any scientific body of national or international standing. Temperature rise is accelerated or tempered by climate feedbacks, such as loss of sunlight-reflecting snow and ice cover, increased water vapour (a greenhouse gas itself), and changes to land and ocean carbon sinks.

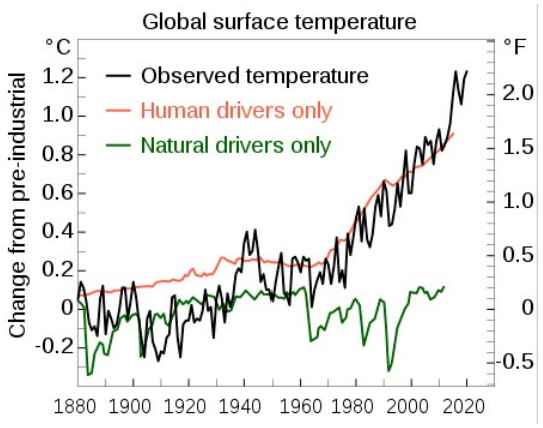


Figure **13.11.1** Observed temperature from NASA versus the 1850-1900 average as a pre-industrial baseline.

The **greenhouse effect** is the process by which radiation from a planet's atmosphere warms the planet's surface to a temperature above what it would be without this atmosphere (Figure **13.11.2**). Radiatively active gases (i.e. greenhouse gases) in a planet's atmosphere radiate energy in all directions. Part of this radiation is directed towards the surface, thus warming it. The intensity of downward radiation – that is, the strength of the greenhouse effect – depends on the amount of greenhouse gases that the atmosphere contains. The temperature rises until the intensity of upward radiation from the surface, thus cooling it, balances the downward flow of energy.

Earth's natural greenhouse effect is critical to supporting life and initially was a precursor to life moving out of the ocean onto land. Human activities, mainly the burning of fossil fuels and clear cutting of forests, have increased the greenhouse effect and caused global warming.

The term *greenhouse effect* is a slight misnomer in the sense that physical greenhouses warm via a different mechanism. The greenhouse effect as an atmospheric mechanism functions through radiative heat loss while a traditional greenhouse as a built structure blocks convective heat loss. The result, however, is an increase in temperature in both cases.

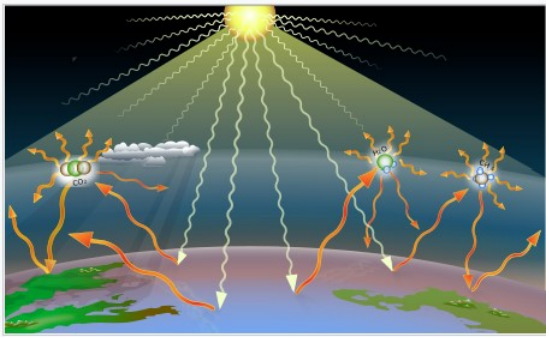


Figure 13.11.2 The greenhouse effect of solar radiation on the Earth's surface caused by emission of greenhouse gases. Source: Wikipedia

Greenhouse Gases and Global Warming

A **greenhouse gas** (sometimes abbreviated **GHG**) is a gas that absorbs and emits radiant energy within the thermal infrared range, causing the greenhouse effect. It's important to realize that **water vapor** (H_2O) is also a greenhouse gas. While humans have little direct impact on water vapor concentrations in the atmosphere, it is still an essential component of the natural greenhouse effect that occurs in our atmosphere. The four major categories of greenhouse gases that have been impacted by humans the most will be discussed in detail below. See Table **13.11.1** for a numeric comparison of these greenhouse gases.

• Carbon dioxide, CO_2

• Methane, CH_4

• Nitrous oxide, N_2O

• Synthetic **fluorinated gases**, including **hydrofluorocarbons** (HFCs), **perfluorocarbons** (PFCs), and **sulfur hexafluoride** (SF_6)

Carbon dioxide (CO_2) is the greenhouse gas responsible for most of the human-caused climate change in our atmosphere. It has the highest concentration in the atmosphere of any of the greenhouse gases that we'll discuss here. Remember that CO_2 is a direct product of both combustion and cellular respiration, causing it to be produced in great quantities both naturally and anthropogenically. Any time biomass or fossil fuels are burned, CO_2 is released. Major anthropogenic sources include: electricity production from coal-fired and natural gas power plants, transportation, and industry (Chapter 4). To get an idea of how CO_2 concentration has changed over time, watch this video compiled by the National Oceanic and Atmospheric Administration (NOAA): http://www.esrl.noaa.gov/gmd/ccgg/trends/history.html. This video contains atmospheric CO_2 concentrations measured directly, dating back to 1958, as well as atmospheric CO_2 concentrations measured indirectly from ice core data, dating back to 800,000 BCE. By 1990, a quantity of over seven billion tons of carbon (equivalent to 26 billion tons of carbon dioxide when the weight of the oxygen atoms are also considered) was being emitted into the atmosphere every year, much of it from industrialized nations. Similar to the action of the naturally existing greenhouse gases, any additional greenhouse gases leads to an increase in the surface temperature of the Earth.

While CO_2 is produced by aerobic cellular respiration, gases such as CH_4 and N_2O are often the products of anaerobic metabolisms. Agriculture is a major contributor to CH_4 emissions. In addition to anaerobic bacteria, methane is also a significant component of natural gas, and is commonly emitted through the mining and use of natural gas and petroleum, in addition to coal mining. Finally, landfills contribute significantly to CH_4 emissions, as the waste put into the landfill largely undergoes anaerobic decomposition as it is buried under many layers of trash and soil. Natural sources of CH_4 include swamps and wetlands, and volcanoes.

The vast majority of N_2O production by humans comes from agricultural land management. While some N_2O is naturally emitted to the atmosphere from soil as part of the nitrogen cycle, human changes in land management, largely due to agricultural practices, have greatly increased N_2O emissions. Some N_2O is also emitted from transportation and industry.

Due to their relatively high concentrations in the atmosphere compared to synthetic gases, CO_2, CH_4, and N_2O, are responsible for most of the human-caused global climate change over the past century. Figure **13.11.2** shows the increases in all three gases since

1750. Ice core data shows us that the atmospheric CO_2 concentration never exceeded 300 ppm before the industrial revolution. As of early 2015, the current atmospheric CO_2 concentration is 400 ppm.

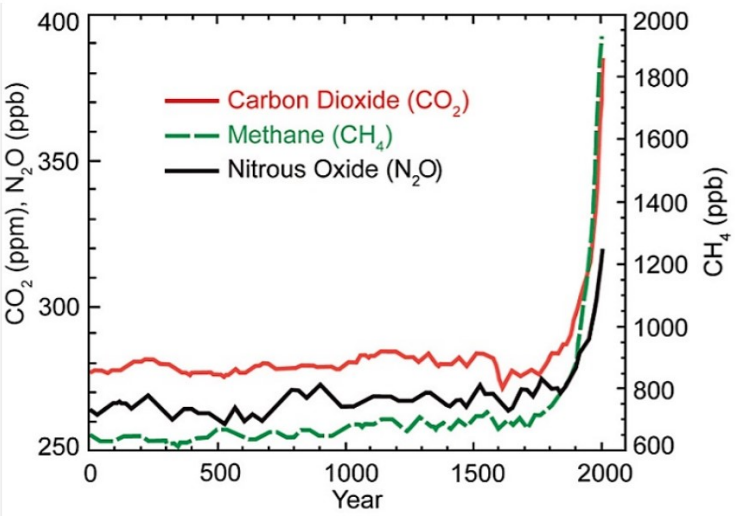


Figure **13.11.2**: Increase in greenhouse gas concentrations in the atmosphere over the last 2,000 years. Increases in concentrations of these gases since 1750 are due to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion molecules of air. Source: USGCRP (2009)

One class of greenhouse gas chemicals that has no natural sources is the fluorinated gases. These include HFCs, PFCs, and SF6, among others. Because these are synthetic chemicals that are only created by humans, these gases were essentially non-existent before the industrial revolution. These synthetic gases are used for a wide variety of applications, from refrigerants to semiconductor manufacturing, and propellants to fire retardants. They tend to have a long lifetime in the atmosphere, as seen in Table **13.11.1**. Some of these chemicals, as well as the older **chlorofluorocarbons** (CFCs), have been phased out by international environmental legislation under the Montreal Protocol. Due to their long lifespan, many of these now banned CFCs remain in the atmosphere. Newer chemical replacements, such as HFCs, provide many of the same industrial applications, but unfortunately have their own environmental consequences.

Just as greenhouse gases differ in their sources and their residence time in the atmosphere, they also differ in their ability to produce the greenhouse effect. This is measured by the **global warming potential**, or GWP, of each greenhouse gas. The GWP of a greenhouse gas is based on its ability to absorb and scatter energy, as well as its lifetime in the atmosphere. Since CO_2 is the most prevalent greenhouse gas, all other greenhouse gases are measured relative to it. As the reference point, CO_2 always has a GWP of 1. Note the very high GWP values of the synthetic fluorinated gases in Table **13.11.1**. This is largely due to their very long residence time in the atmosphere. Also note the higher GWP values for CH_4 and N_2O compared to CO_2.

Table **13.11.1**. Comparision of Greenhouse Gases.

Greenhouse gas	Chemical formula or abbreviation	Lifetime in atmosphere	Global warming potential (100-year)
Carbon dioxide	CO_2	Variable	1
Methane	CH_4	12 years	28-36
Nitrous oxide	N_2O	114 years	298
Hydrofluorocarbons	Abbreviation: HFCs	1-270 years	12-14,800
Perfluorocarbons	Abbreviation: PFCs	2,600-50,000 years	7,390
Sulfur hexafluoride	SF6	3,200 years	22,800

Other climate influencers

In addition to greenhouse gases, other manmade changes may be forcing climate change. Increases in near-surface ozone from internal combustion engines, aerosols such as carbon black, mineral dust and aviation-induced exhaust are acting to raise the surface temperature. This primarily occurs due to a decrease in the **albedo** of light-colored surfaces by the darker-colored carbon black, soot, dust, or particulate matter. As you know, it is more comfortable to wear a white shirt on a hot summer day than a black shirt. Why is this? Because the lighter-colored material bounces more solar radiation back toward space than the darker-colored material does, allowing it to stay cooler. The darker-colored material absorbs more solar radiation, increasing its temperature. Just as the white shirt has a higher albedo than the black shirt, light-colored objects in nature (such as snow) have a higher albedo than dark-colored objects (such as soot or dust). As humans increase the amount of carbon black, soot, dust, and particulates in the atmosphere, we decrease the albedo of light-colored surfaces, causing them to absorb more solar radiation and become warmer than they would without human influence. An example of this can be seen in the snow on Figure **13.11.3**.



Figure **13.11.3**: A photograph of the extreme dust deposition from the deserts of the Colorado Plateau onto the Colorado Rockies snowpack in 2009. Taken from the high point of the Senator Beck Basin in the San Juan Mountains, it captures the extent of the impact of darkening in which the snow albedo dropped to about 30%, more than doubling the absorption of sunlight. Credit: S. McKenzie Skiles, Snow Optics Laboratory, NASA/JPL

Consequences of Climate Change

We will only discuss some of the consequences of climate change in this section, including changes in temperature, precipitation, ocean level, and ocean acidity. There are many more changes that have been seen, and are projected to continue in the future. These include: changes in the amount and distribution of ice and snow, changes in seasonality, ecosystem shift, and habitat changes of plant and animal populations, in addition to others. For more information about these consequence of climate change, visit this site: http://www.epa.gov/climatechange/sci...ors/index.html.

Temperature and precipitation

Temperature and **precipitation** are the two most direct impacts on the Earth's climate due to climate change. By now, you should already understand why an increase in greenhouse gas levels in the atmosphere causes an increase in temperature. But why does it also impact precipitation patterns? As you already know, water vapor is an important component of the Earth's atmosphere . As the air in the troposphere warms and cools, the amount of water vapor that it holds changes dramatically. Here in Georgia, we have very hot and humid summers. The high summer humidity in this region is possible due to the increased capability warm air has to

hold water vapor. Simply put, warmer air can hold more water than cooler air. As air cools, its ability to hold water vapor decreases, and any excess water will leave the air as liquid water. A great example of this is the formation of dew on surfaces overnight. During the day, the temperature is warmer than it is at night, and the air has a relatively high holding capacity for water vapor. When the sun sets, the air cools, decreasing its capacity to hold water vapor. That extra water must go somewhere, and it does that by accumulating on surfaces. Similarly, when warm and cool air fronts collide, the chances for rain and thunderstorms increase. Furthermore, an increase in temperature enhances evaporation occurring at the Earth's surface. This increased evaporation leads to greater concentrations of water vapor in the atmosphere which can lead to increased precipitation.

The change in temperature that we have already seen in the Earth's average atmospheric temperature is relatively small (about1.2 °C, according to Figure 7.5.1). However, as with many of the aspects of climate change, the potential for greater changes increases dramatically as time progresses in the future. This can be seen in Figure **13.11.4**, which displays a model of the predicted temperature increase. Notice that these changes occur relatively rapidly, and are not uniform across the globe. What might be some of the reasons for this?

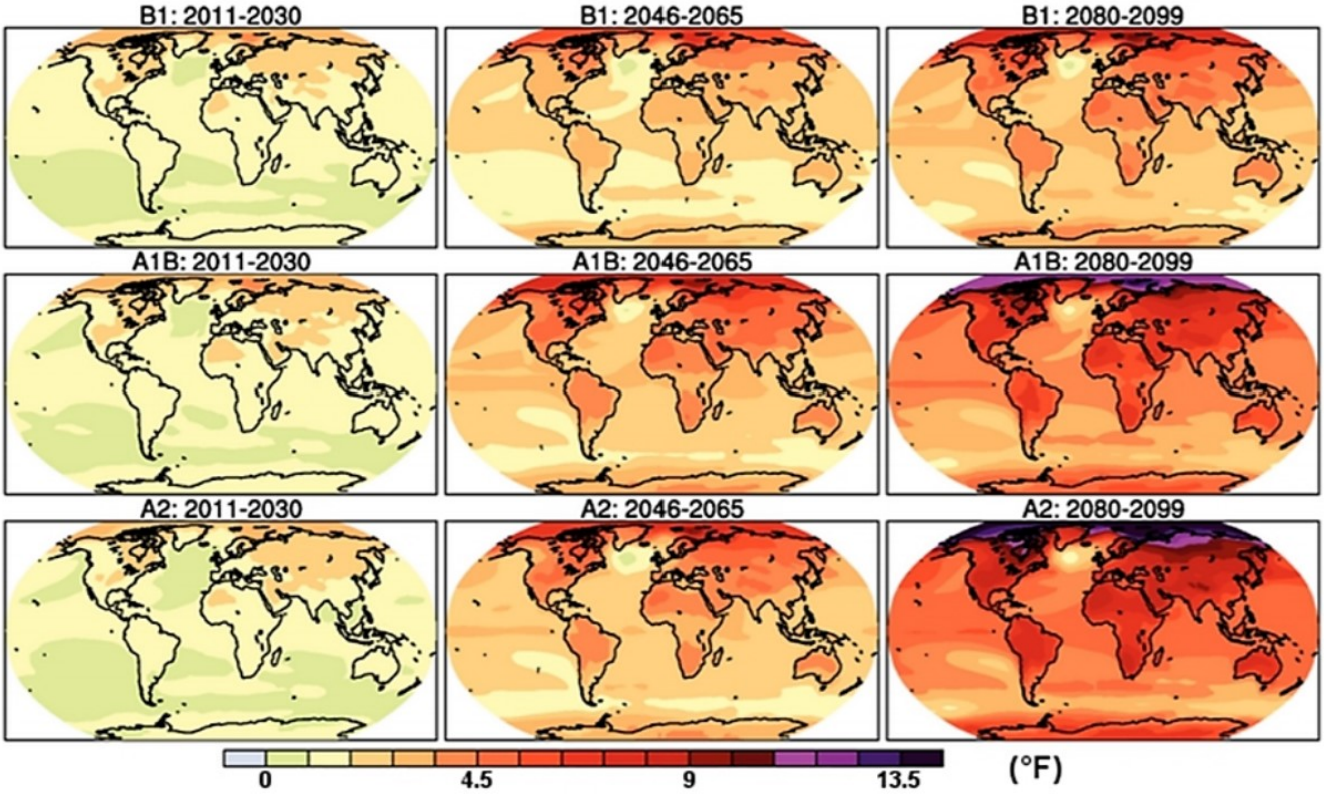


Figure **13.11.4**: Projected changes in global average temperatures under three emissions scenarios (rows) for three different time periods (columns). Changes in temperatures are relative to 1961- 1990 averages. The scenarios come from the IPCC Special Report on Emissions Scenarios: B1 is a low emissions scenario, A1B is a medium-high emissions scenario, and A2 is a high emissions scenario. Source: IPCC Working Group I: The Physical Science Basis, 2007.

Changes in precipitation occur due to a variety of factors, including changes in atmospheric water vapor content due to changing temperature, as discussed above. Also at play is the heightened **evaporation** rate of water on Earth's surface under warmer temperatures. More evaporation leads to more precipitation. Finally, shifts in wind patterns impact the distribution of precipitation events. As you can see in Figure **13.11.5**, there are some areas of the globe that are expected to have an increase in precipitation, while others are expected to have a dramatic decrease. Some major population centers projected to have a moderate to severe precipitation increase include (population estimates of the metropolitan area given in parentheses): New York, United States (20.1 million); Bogotá, Colombia (12.1 m.); and Manila, Philippines (11.9 m.). What sort of challenges might these cities face in the future as they deal with this change in their climate?

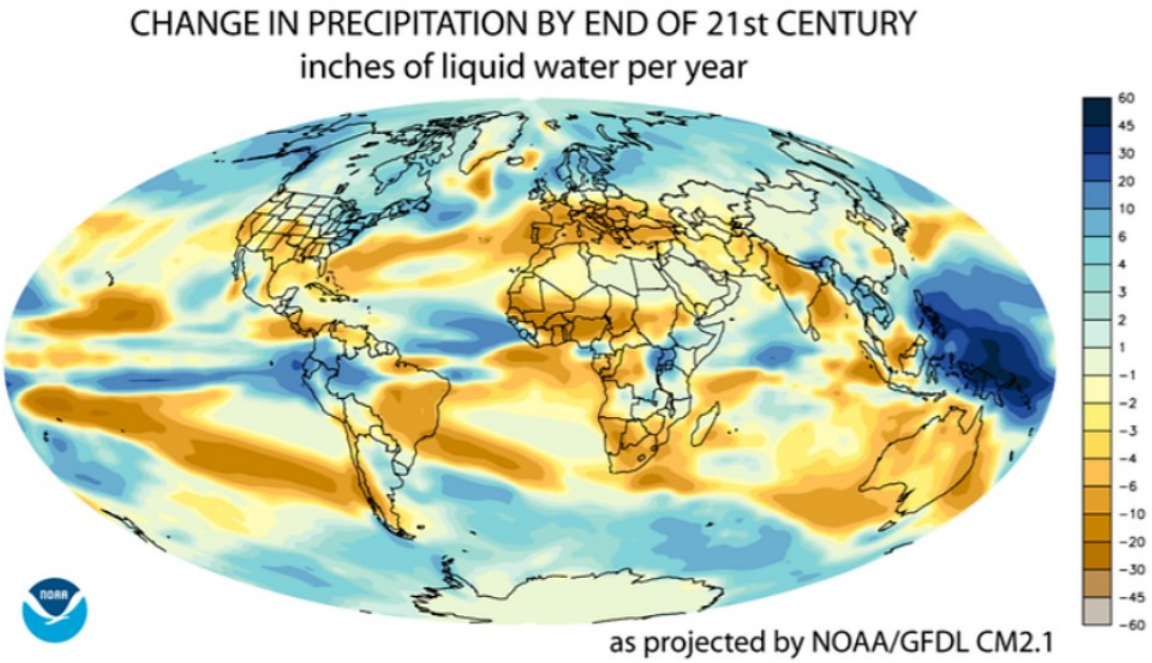


Figure **13.11.5** The plotted precipitation differences were computed as the difference between the 2081 to 2100 20-year averages minus the 1951 to 2000 50-year average. Blue areas project increases in precipitation; brown areas project decreases.

In contrast, many more major metropolitan areas are projected to have a moderate to severe precipitation decrease (droughts) by the end of the 21st century. These include Delhi, India (21.8 m.); Lagos, Nigeria (21 m.); São Paulo, Brazil (20.9 m.); Kolkata, India (14.6 m.); Istanbul, Turkey (14.4 m.); Los Angeles, United States (13.3 m.); Rio de Janeiro, Brazil (12 m.); Paris, France (12 m.); and Lahore, Pakistan (11.3 m.). The largest challenge that these areas are likely to face is a dwindling water supply for drinking and agriculture. See Chapter 8 for more detail on challenges faced by societies to supply clean, reliable water to their populations and farms.

Additional challenges may be felt by all areas of the world with regard to changes in the seasonality or timing of precipitation, as well the form in which precipitation falls (e.g., mist or downpour; rain, ice, or snow). All of these factors affect the availability of soil water for plants, the flow of rivers and streams, and the overall accessibility of water worldwide. Furthermore, scientists predict an increase in the number and severity of storms as climate change progresses. For a full discussion of the potential impacts of this, see the assigned article.

Sea level rise While we know that water continuously cycles around the world, and that the overall quantity of water on Earth will not change due to global climate change, the distribution of this water is changing. In particular, oceans are increasing in volume while land ice stores (such as **glaciers**) are decreasing. This contributes to an increase in sea level worldwide (Figure **13.11.6**).

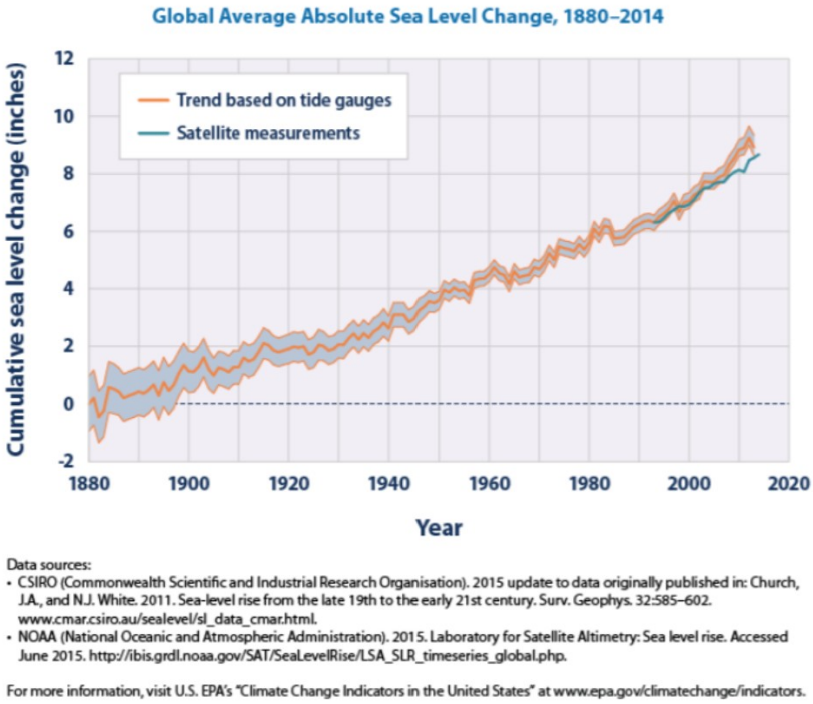


Figure **13.11.6**: *This graph shows average absolute cumulative changes in sea level for the world's oceans since 1880, based on a combination of tide gauge measurements and recent satellite measurements. The shaded band shows the likely range of values, based on the number of measurements collected and the precision of the methods used.*

From the data in Figure **13.11.6**, we see that sea level has increased at an average of 0.06 inches (0.15 cm) per year over the time period shown above. Most of this rise, however, has occurred within the most recent decades. The rate of increase has gone up to between 0.11 to 0.14 inches (0.28 to 0.36 cm) per year since 1993. There are two forces causing sea level to rise, both caused by climate change. First, the increased global temperature has caused increased ice melting in many regions of the globe. Melting **land ice** (such as the glacier shown in Figure **13.11.7**) contributes to sea level rise because water that used to be stored in ice sitting on top of land becomes running water which reaches the ocean through **runoff.** We also observe **sea ice** melting (see http://www.epa.gov/climatechange/sci ence/indicators/index.html for data and figures). Sea ice, such as the ice that covers the arctic regions of the Northern Hemisphere, has no land underneath it. When it melts, the water stays in the same locations, and the overall sea level does not change.



Figure 13.11.7: Glacier Retreat

The second factor that influences sea level rise is a phenomenon called thermal expansion. Due to the physical properties of water, as water warms, its density decreases. A less dense substance will have fewer molecules in a given area than a more dense substance (see Chapter 1 supplemental material). This means that as the overall temperature of the oceans increases due to global climate change, the same amount of water molecules will now occupy a slightly larger volume. This may not seem significant, but considering the 1.3 billion trillion liters (264 billion gallons) of water in the ocean, even a small change in density can have large effects on sea level as a whole.

Scientists have already documented sea level rise in some areas of the world, including one familiar to most of us: the Southeastern United States. Figure **13.11.8** depicts the measured land area lost due to increasing sea level since 1996. Note that the Southeast (defined here as the Atlantic coast of North Carolina south to Florida) is particularly susceptible to land area loss due to the gently sloping nature of our coastline. Moving northward into the Mid-Atlantic States (defined here as Virginia north to Long Island, New York), coastal habitats tend to have a steeper geography, which protects against some losses.

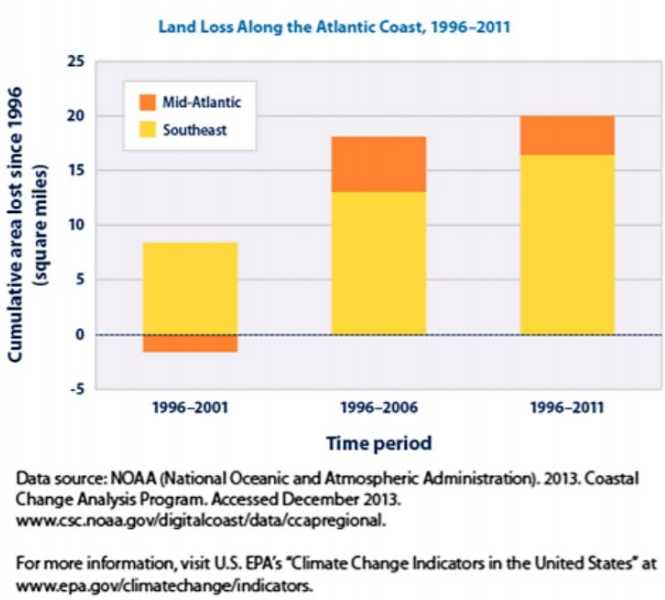


Figure **13.11.8**: This graph shows the net amount of land converted to open water along the Atlantic coast during three time periods: 1996–2001, 1996–2006, and 1996–2011. The results are divided into two regions: the Southeast and the Mid-Atlantic. Negative numbers show where land loss is outpaced by the accumulation of new land.

While the ecological effects of sea level rise remain in the United States, we don't project any catastrophic loss of life, property, or livelihood for some time. This is, in part, due to large investments that we have made in infrastructure to protect our cities and farmlands. This is not the case in many areas of the world. For a discussion of the impacts of sea level rise on less industrialized nations of Bangladesh, Maldives, Kiribati, and Fiji, review the required article reading.

Ocean acidification

Dissolved CO_2 is essential for many organisms, including shell-building animals and other organisms that form a hard coating on their exterior (e.g., shellfish, corals, Haptophyte algae). This hard coating is built out of aragonite, a mineral form of the molecule calcium carbonate, $CaCO_3$. These organisms rely on the formation of carbonate ions (see Chapter 1 supplemental material for information on ions), CO_3^{2-}, from dissolved CO_2, through a natural, chemical reaction that occurs. This takes place through a chain-reaction equation, where bicarbonate (HCO_3^-) is formed as an intermediate, and hydrogen ions (H^+) are generated (equations **13.11.1** and **13.11.2**).

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

To have a better visualization of this process, follow along with the interactive graphic at: http://www.whoi.edu/home/oceanus_ima...ification.html.

As you can see, both equations **13.11.1** and **13.11.2** each produce one H^+. This is significant to water chemistry because an increase in H+ concentration means a decrease in the pH of the water. You can see in Figure **13.11.9** that a lower pH means that the liquid is more acidic. As shown in the interactive graphic, an increase in CO_2 in the atmosphere causes additional CO_2 to be dissolved in the ocean. This means that more CO_2 in the atmosphere leads to more acidic ocean environments.

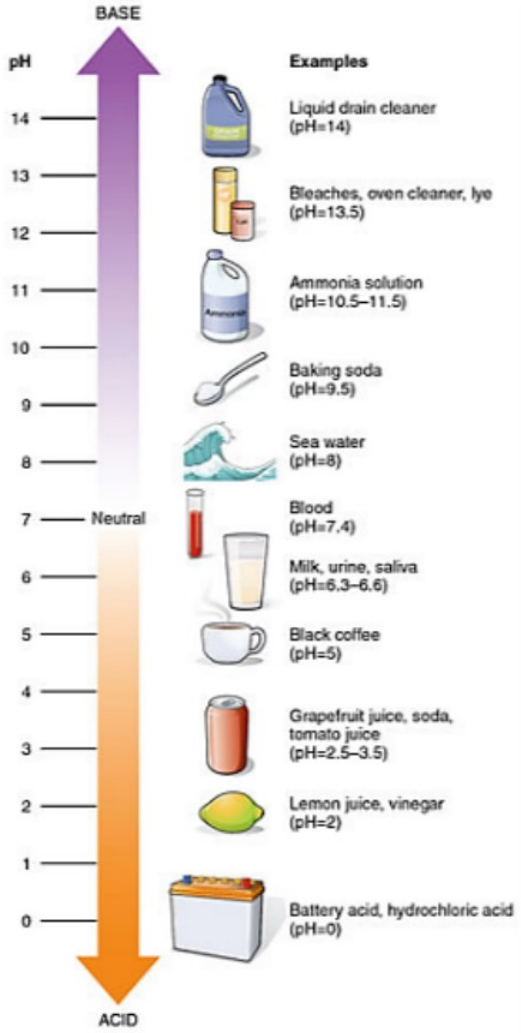


Figure **13.11.9**: The pH scale and relative acidity. Illustration from Anatomy & Physiology, Connexions Web site. http://cnx.org/content/col11496/1.6/, Jun 19, 2013.

Unfortunately for shell-building animals, the buildup of H^+ in the more acidic ocean environment blocks the absorption of calcium and CO_3^{2-}, and makes the formation of aragonite more difficult. An aragonite deficit is already being documented in many of the world's oceans, as shown in Figure **13.11.10**.

The increasing acidity of the world's oceans is resulting in habitat changes across the globe. This is only expected to worsen as atmospheric CO_2 levels continue to increase. Many organisms, including the corals that are the foundation species of the beautiful coral reefs, are very sensitive to changes in ocean pH. Scientists have documented cases of ecosystem destruction through coral bleaching, caused by the effects of climate change including ocean acidification and increased temperature. For more information, visit the NOAA Coral Reef Conservation Program website: coralreef.noaa.gov/threats/climate/.

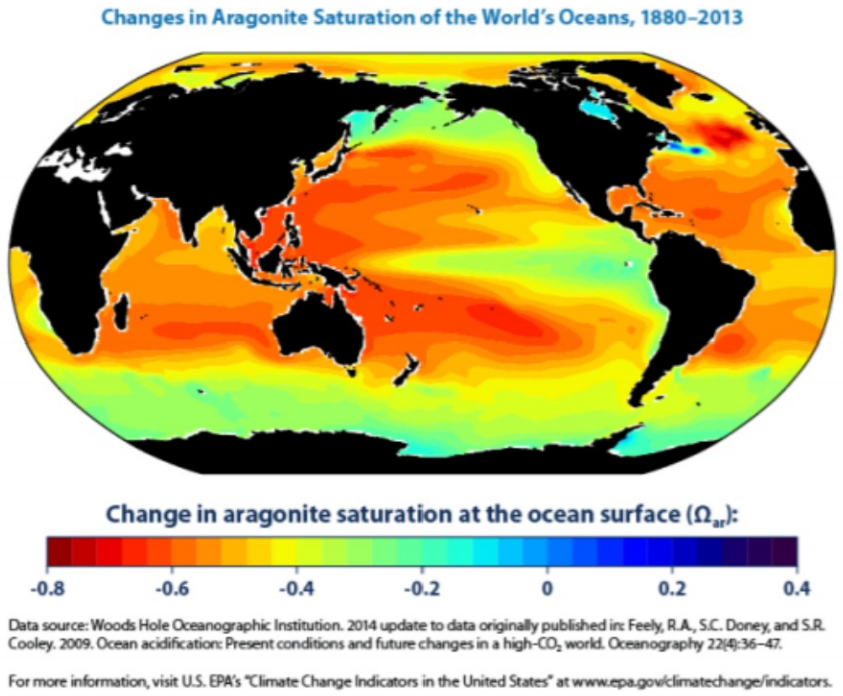


Figure **13.11.10**: This map shows changes in the aragonite saturation level of ocean surface waters between the 1880s and the most recent decade (2004–2013). Aragonite is a form of calcium carbonate that many marine animals use to build their skeletons and shells. A negative change represents a decrease in saturation.

Climate Strategies

While the situation surrounding global climate change is in serious need of our attention, it is important to realize that many scientists, leaders, and concerned citizens are making solutions to climate change part of their life's work. The two solutions to the problems caused by climate change are **mitigation** and **adaptation**, and we will likely need a combination of both in order to prosper in the future.

Adaptation strategies

We know that climate change is already occurring, as we can see and feel the effects of it. For this reason, it is essential to also adapt to our changing environment. This means that we must change our behaviors in response to the changing environment around us. Some adaptation strategies are discussed in the required article reading.

Adaption strategies will vary greatly by region, depending on the largest specific impacts in that area. For example, in the city of Delhi, India, a dramatic decrease in rainfall is projected over the next century (Figure 7.6.2). This city will likely need to implement policies and practices relating to conservation of water, for example: rainwater harvesting, water re-use, and increased irrigation efficiency. Rain-limited cities near oceans, such as Los Angeles, California may choose to use desalination to provide drinking water to their citizens. **Desalination** involves taking the salt out of seawater to make it potable (Chapter 14).

Cities with low elevations near oceans may need to implement adaptation strategies to rising sea levels, from seawalls and levees to relocation of citizens. One adaptations strategy gaining use is the creation or conservation of **wetlands**, which provide natural protection against storm surges and flooding.

Mitigation strategies

In general, a strategy to mitigate climate change is one that reduces the amount of greenhouse gases in the atmosphere or prevents additional emissions. Mitigations strategies attempt to "fix" the problems caused by climate change. Governmental regulations regarding fuel efficiency of vehicles is one example of an institutionalized mitigation strategy already in place in the United States and in many other countries around the world. Unlike some other countries, there are no **carbon taxes** or charges on burning fossil

fuels in the United States. This is another governmental mitigation strategy that has been shown to be effective in many countries including India, Japan, France, Costa Rica, Canada, and the United Kingdom.

In addition to government measures and incentives, technology can also be harnessed to mitigate climate change. One strategy for this is the use of **carbon capture and sequestration** (CCS). Through CCS, 80-90% of the CO_2 that would have been emitted to the atmosphere from sources such as a coal-fired power plant is instead captured and then stored deep beneath the Earth's surface. The CO_2 is often injected and sequestered hundreds of miles underground into porous rock formations sealed below an impermeable layer, where it is stored permanently (Figure **13.11.11**).

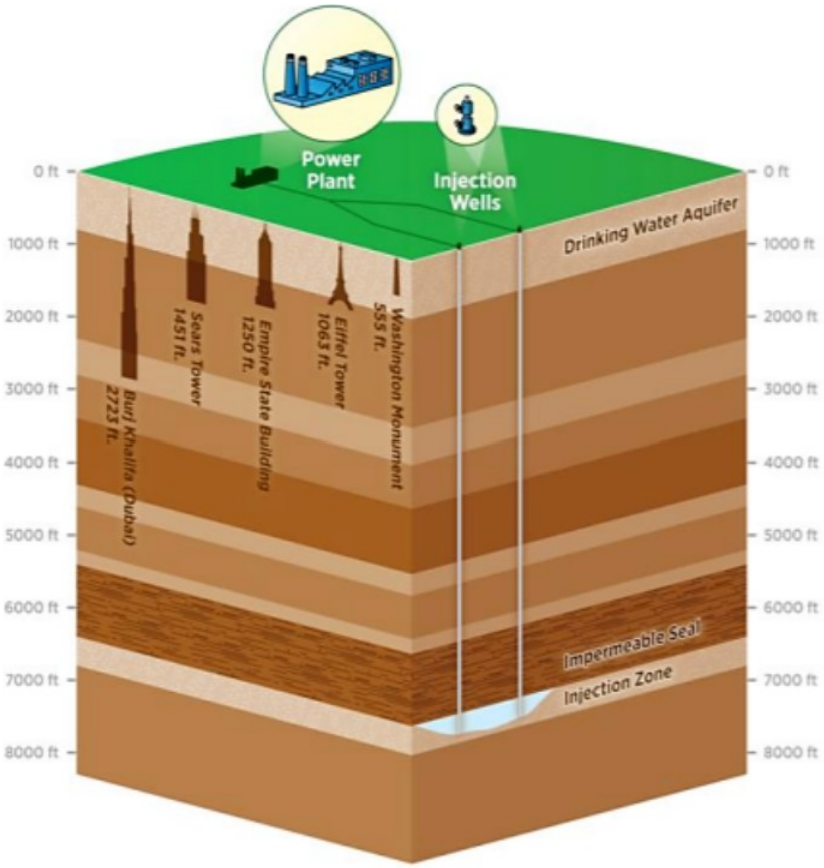


Figure **13.11.11**: Carbon capture and sequestration schematic with landmarks shown to scale for depth reference. Source: US EPA.

Scientists are also looking into the use of soils and vegetation for carbon storage potential. Proper management of soil and forest ecosystems has been shown to create additional carbon sinks for atmospheric carbon, reducing the overall atmospheric CO_2 burden. Increasing soil carbon further benefits communities by providing better-quality soil for agriculture and cultivation.

Technologies related to alternative energy sources (Chapter 15) mitigate climate change by providing people with energy not derived from the combustion of fossil fuels. Finally, simple activities such as energy conservation, choosing to walk or bike instead of driving, and disposing of waste properly are activities that, when done by large numbers of people, actively mitigate climate change by preventing carbon emissions.

Take a moment to identify ways that you personally can be involved in the mitigation of or adaptation to climate change. What changes can you make in your own life to prevent excess carbon emissions? Similar to your ecological footprint, which you should have already calculated in lab, you can also calculate your carbon footprint. Use the EPA's carbon footprint calculator to do so, and investigate the Reduce Your Emissions section to find ways to decrease your carbon footprint.

Recommendations from the US Environmental Protection Agency

Figure **13.11.12** list various technologies and approaches that companies and individuals can adapt to reduce greenhouse gases. Technologies related to alternative energy sources mitigate climate change by providing people with energy not derived from the combustion of fossil fuels. Finally, simple activities such as energy conservation, choosing to walk or bike instead of driving, and disposing of waste properly are activities that, when done by large numbers of people, actively mitigate climate change by preventing carbon emissions.

Solutions for Transportation Air Pollution

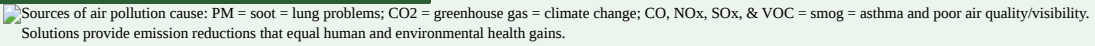


Figure **13.11.6** *Sources and solutions for transportation air pollution. Image: EPA*

Solutions for transportation air pollution, emission reductions, can lead to cleaner air and better health.

- Catalytic converters in conjunction with unleaded gasoline and low sulfur levels significantly reduce hydrocarbon and nitrogen oxide emissions.
- Fuel standards reduce exposure to pollutants like lead and benzene. Renewable fuels reduce CO_2 emissions.
- Engine technologies like computer controls, variable valve timing, multi-valve engines, turbo charging and gasoline direct injection improve fuel economy and reduce CO_2 emissions.
- Transmission technologies like 7+ speeds, dual clutch transmissions, (DCTs), and continuously variable transmissions (CVTs) improve fuel economy and reduce CO_2 emissions.
- Diesel filters reduce particulate matter from on road and off road diesel engines. Alternative vehicle technologies like plug-in electric vehicles and fuel cells equals zero tailpipe emissions.
- Better transportation planning for passengers and freight reduce emissions and fuel use.

Summary

- Gases that trap heat in the atmosphere are called greenhouse gases.
- The greenhouse effect is the process by which radiation from a planet's atmosphere warms the planet's surface to a temperature above what it would be without this atmosphere.
- Global warming refers to the increase in the average temperature of the Earth’s atmosphere due to elevated greenhouse gas concentrations, heightening the greenhouse effect.
- Climate change includes both global warming driven by human-induced emissions of greenhouse gasesand the resulting large-scale shifts in weather patterns.
- Greenhouse gases differ in their ability to produce the greenhouse effect as measured by the global warming potential, or GWP. A molecule of CH_4 is about 28 times more effective than one of CO_2 at absorbing infrared radiation, while N_2O is 298 times more effective . The synthetic fluorinated gases are evn much higher (in the thousands). This is largely due to their very long residence time in the atmosphere.

- Different technologies and approaches recommended by the US EPA to to reduce human greenhouse emmissions were provided.

Contributors and Attributions

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- Libretext: Introduction to Environmental Science (Zendher et al.)
- US EPA
- Wikipedia

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CHAPTER OVERVIEW

14: Liquids, Solids, and Intermolecular Forces

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In Chapter 6, we discussed the properties of gases. In this chapter, we consider some properties of liquids and solids. As a review, the table below lists some general properties of the three phases of matter.

Phase	Shape	Density	Compressibility
Gas	fills entire container	low	high
Liquid	fills a container from bottom to top	high	low
Solid	rigid	high	low

14.1: Prelude to Solids and Liquids
14.2: Interactions between Molecules
14.3: Properties of Liquids and Solids
14.4: Surface Tension and Viscosity
14.5: Evaporation and Condensation
14.6: Melting, Freezing, and Sublimation
14.7: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole
14.8: Cleaning with Soap

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14.1: Prelude to Solids and Liquids

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 **14.1.1** 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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14.2: Interactions between Molecules

In the winter, many people find the snow and ice beautiful; they enjoy getting out to ski or ice-skate. When the snow melts, however, the roads get very sloppy and messy. Some people look forward to spring, when the ice and snow are gone and the weather is warmer. All of these events and factors are dependent on the melting point of a solid and the freezing point of a liquid.

Melting Point

Solids are similar to liquids in that both are condensed states, with particles that are far closer together than those of a gas. However, while liquids are fluid, solids are not. The particles of most solids are packed tightly together in an orderly arrangement. The motion of individual atoms, ions, or molecules in a solid is restricted to **vibrational motion** about a fixed point. Solids are almost completely **incompressible** and are the densest of the three states of matter.

As a solid is heated, its particles vibrate more rapidly as it absorbs kinetic energy. Eventually, the organization of the particles within the solid structure begins to break down and the solid starts to melt. The **melting point** is the temperature at which a solid changes into a liquid. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid. As with boiling points, the melting point of a solid is dependent on the strength of those attractive forces. Sodium chloride (NaCl) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at $801°\mathrm{C}$. Ice (solid $\mathrm{H_2O}$) is a molecular compound of molecules that are held together by hydrogen bonds. Though hydrogen bonds are the strongest of the intermolecular forces, the strength of hydrogen bonds is much less than that of ionic bonds. The melting point of ice is 0 °C.



Figure **14.2.1**: Melting ice cubes illustrate the process of this phase transition. (Public Domain; Moussa).

The melting point of a solid is the same as the **freezing point** of the liquid. At that temperature, the solid and liquid states of the substance are in equilibrium. For water, this equilibrium occurs at $0°\mathrm{C}$.

$$\mathrm{H_2O}\,(s) \rightleftharpoons \mathrm{H_2O}\,(l)$$

We tend to think of solids as those materials that are solid at room temperature. However, all materials have melting points of some sort. Gases become solids at extremely low temperatures, and liquids will also become solid if the temperature is low enough. The table below gives the melting points of some common materials.

Table **14.2.1**: Melting Points of Common Materials

Materials	Melting Point (°C)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961
Pure gold	1063
Iron	1538

Summary

The melting point is the temperature at which a solid changes into a liquid. Intermolecular forces have a strong influence on melting point.

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14.3: Properties of Liquids and Solids

Learning Objectives

- Describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.



Figure **14.3.1**: A crystalline arrangement of quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. (Source: Wikipedia.)

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure **14.3.1**. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.



Figure **14.3.2**: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. (Source: Wikipedia.)

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

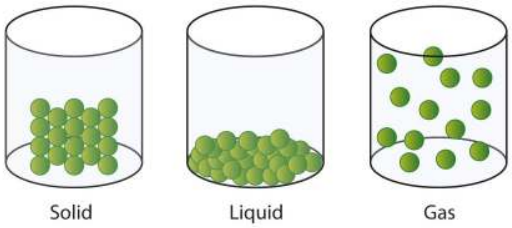


Figure **14.3.3**: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure **14.3.3** shows the differences among solids, liquids, and gases at the molecular level, while Table **14.3.1** lists the different characteristics of these states.

Table **14.3.1**: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

✔ Example 14.3.1

What state or states of matter does each statement describe?

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

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

? Exercise 14.3.1

What state or states of matter does each statement describe?

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

Answer a

solid

Answer b

gas

Answer c

liquid or gas

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface; life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. In colder weather, lakes and rivers freeze from the top, allowing animals and plants to continue to live underneath. Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water's influence on the world around us is affected by these properties. Isn't it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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14.4: Surface Tension and Viscosity

Learning Objectives

- Explain the how the surface tension of a liquid relates to intermolecular forces.

The next time you are by a still body of water, take a close look at what is scooting along on the surface. You may see insects seemingly floating on top of the water. These creatures are known by a variety of names including water skaters, water striders, pond skaters, and other equally descriptive names. They take advantage of a property called surface tension to stay above the water and not sink. The force they exert downward is less than the forces exerted among the water molecules on the surface of the pond, so the insect does not penetrate beneath the surface of the water.

Surface Tension

Molecules within a liquid are pulled equally in all directions by intermolecular forces. However, molecules at the surface are pulled downwards and sideways by other liquid molecules, but not upwards away from the surface. The overall effect is that the surface molecules are pulled into the liquid, creating a surface that is tightened like a film (Figure **14.4.1*A***). The **surface tension** of a liquid is a measure of the elastic force in the liquid's surface. Liquids that have strong intermolecular forces, like the hydrogen bonding in water, exhibit the greatest surface tension. Surface tension allows objects that are denser than water, such as the paper clip shown in B in the figure below, to nonetheless float on its surface. It is also responsible for the beading up of water droplets on a freshly waxed car, because there are no attractions between the polar water molecules and the nonpolar wax.

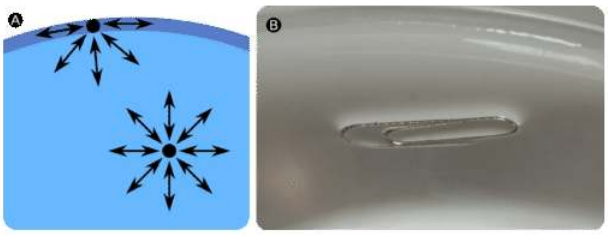


Figure **14.4.1**: (A) Molecules at the surface of a liquid are pulled downwards into the liquid, creating a tightened surface. (B) Surface tension allows a paper clip to float on water's surface.

Other liquids, such as diethyl ether, do not demonstrate strong surface tension interactions. The intermolecular forces for the ether are the relatively weak dipole-dipole interactions that do not draw the molecules together as tightly as hydrogen bonds would.

Summary

- The surface tension of a liquid is a measure of the elastic force in the liquid's surface.
- Liquids with strong intermolecular forces have higher surface tensions than liquids with weaker forces.

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14.5: Evaporation and Condensation

Learning Objectives

- Explain how intermolecular forces affect rates of vaporization, evaporation, and condensation.

On the roof of the house in the picture below is a device known as a "swamp cooler". This piece of equipment traces its origin back to the ancient Egyptians who hung wet blankets across the doors of their homes. As the warm air passed through the blankets, water would evaporate and cool the air. The royalty went one step further and had servants fan wet cloths over jugs of water to get more evaporation and cooling.



Figure 14.5.1: A home with a swamp cooler attached to the roof.

The origin of the term "swamp cooler" is not known - they certainly don't work in a swamp. Best conditions for cooling include a high temperature (over 80°F) and a low humidity (preferably less than 30%). These coolers work well in desert areas, but don't provide any cooling in the humid areas of the country.

Evaporation

A puddle of water left undisturbed eventually disappears. The liquid molecules escape into the gas phase, becoming water vapor. **Vaporization** is the process in which a liquid is converted to a gas. **Evaporation** is the conversion of a liquid to its vapor below the boiling temperature of the liquid. If the water is instead kept in a closed container, the water vapor molecules do not have a chance to escape into the surroundings and so the water level does not change. As some water molecules become vapor, an equal number of water vapor molecules condense back into the liquid state. **Condensation** is the change of state from a gas to a liquid.

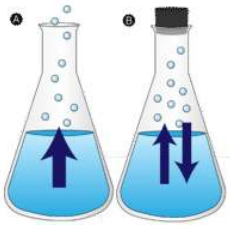


Figure 14.5.2: Evaporation (A) and condensation (B).

In order for a liquid molecule to escape into the gas state, the molecule must have enough kinetic energy to overcome the intermolecular attractive forces in the liquid. Recall that a given liquid sample will have molecules with a wide range of kinetic energies. Liquid molecules that have this certain threshold kinetic energy escape the surface and become vapor. As a result, the liquid molecules that remain now have lower kinetic energy. As evaporation occurs, the temperature of the remaining liquid decreases. You have observed the effects of evaporative cooling. On a hot day, the water molecules in your perspiration absorb body heat and evaporate from the surface of your skin. The evaporating process leaves the remaining perspiration cooler, which in turn absorbs more heat from your body.

A given liquid will evaporate more quickly when it is heated. This is because the heating process results in a greater fraction of the liquid's molecules having the necessary kinetic energy to escape the surface of the liquid. The figure below shows the kinetic

energy distribution of liquid molecules at two temperatures. The numbers of molecules that have the required kinetic energy to evaporate are shown in the shaded area under the curve at the right. The higher temperature liquid (T_2) has more molecules that are capable of escaping into the vapor phase than the lower temperature liquid (T_1).

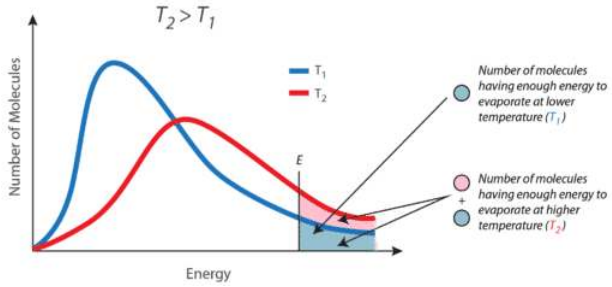


Figure 14.5.3: Kinetic energy distribution curves for a liquid at two temperatures T_1 and T_2. The shaded area represents the molecules with enough kinetic energy to escape the liquid and become vapor.

At 29,029 feet (8848 m), Mount Everest in the Himalayan range on the border between China and Nepal is the highest point on the earth. Its altitude presents many practical problems to climbers. The oxygen content of the air is much lower than at sea level, making it necessary to bring oxygen tanks along (although a few climbers have reached the peak without oxygen). One other problem is that of boiling water for cooking food. Although water boils at 100°C at sea level, the boiling point on top of Mount Everest is only about 70°C. This difference makes it very difficult to get a decent cup of tea (which definitely frustrated some of the British climbers).

Boiling

As a liquid is heated, the average kinetic energy of its particles increases. The rate of evaporation increases as more and more molecules are able to escape the liquid's surface into the vapor phase. Eventually a point is reached when the molecules all throughout the liquid have enough kinetic energy to **vaporize**. At this point the liquid begins to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure. The figure below illustrates the boiling of liquid.

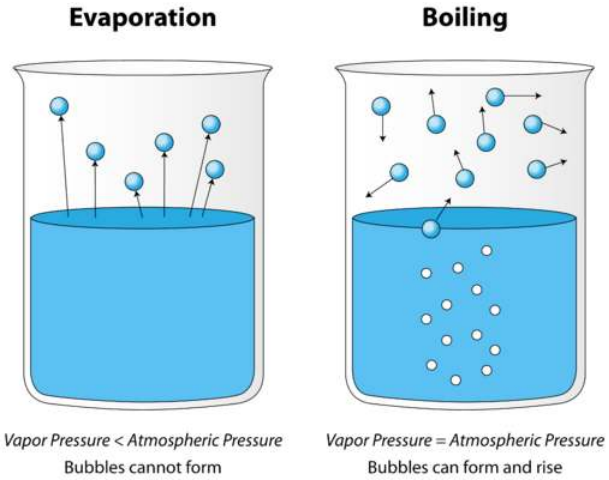


Figure 14.5.4: Comparison between evaporation and boiling.

In the picture on the left, the liquid is below its boiling point, yet some of the liquid evaporates. On the right, the temperature has been increased until bubbles begin to form in the body of the liquid. When the vapor pressure inside the bubble is equal to the external atmospheric pressure, the bubbles rise to the surface of the liquid and burst. The temperature at which this process occurs is the boiling point of the liquid.

The normal boiling point is the temperature at which the vapor pressure of the liquid is equal to standard pressure. Because atmospheric pressure can change based on location, the boiling point of a liquid changes with the external pressure. The normal boiling point is a constant because it is defined relative to the standard atmospheric pressure of 760 mm Hg (or 1 atm or 101.3 kPa).

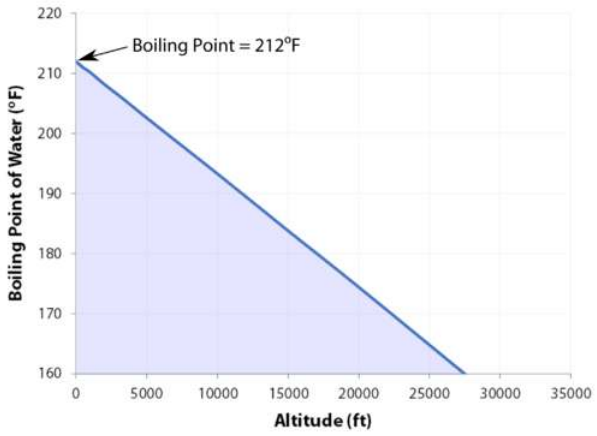


Figure **14.5.5**: Influence of altitude on the boiling point of water.

Summary

- The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- As the altitude increases, the boiling point decreases.
- Evaporation is the conversion of a liquid to its vapor below the boiling temperature of the liquid.
- Condensation is the change of state from a gas to a liquid.
- As the temperature increases, the rate of evaporation increases.

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14.6: Melting, Freezing, and Sublimation

Learning Objectives

- Define melting, freezing, and sublimation.

Depending on the surrounding conditions, normal matter usually exists as one of three *phases*: solid, liquid, or gas.

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid, or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid, or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H_2O) as an example. On the Celsius scale, H_2O has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of H_2O can coexist. However, if heat is added, some of the solid H_2O will melt and turn into liquid H_2O. If heat is removed, the opposite happens: some of the liquid H_2O turns into solid H_2O. A similar process can occur at 100°C: adding heat increases the amount of gaseous H_2O, while removing heat increases the amount of liquid H_2O (Figure **14.6.1**).



Figure **14.6.1**: The Boiling Point of Water. Nucleate boiling of water over a kitchen stove burner. (Source: Wikipedia). Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

Second, the temperature of a substance does not change as the substance goes from one phase to another. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider H_2O as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of H_2O can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{fus} \tag{14.6.1}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{fus} \tag{14.6.2}$$

where m is the mass in grams and ΔH_{fus} is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap} \tag{14.6.3}$$

where n is the number of moles) and ΔH_{vap} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{vap} \tag{14.6.4}$$

where m is the mass in grams and ΔH_{vap} is expressed in energy/gram.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids.

Example 14.6.1

How much heat is necessary to melt 55.8 g of ice (solid H_2O) at 0°C? The heat of fusion of H_2O is 79.9 cal/g.

Solution

We can use the relationship between heat and the heat of fusion (Eq. **14.6.1**b) to determine how many joules of heat are needed to melt this ice:

$$\begin{aligned}\text{heat} &= m \times \Delta H_{fus} \\ &= (55.8\ \cancel{g}) \left(\frac{79.9\ cal}{\cancel{g}} \right) \\ &= 4,460\ cal\end{aligned}$$

Exercise 14.6.1

How much heat is necessary to vaporize 685 g of H_2O at 100°C? The heat of vaporization of H_2O is 540 cal/g.

Table **14.6.1** lists the heats of fusion and vaporization for some common substances. Note the units on these quantities; when you use these values in problem solving, make sure that the other variables in your calculation are expressed in units consistent with the units in the specific heats, or the heats of fusion and vaporization.

Table **14.6.1**: Heats of Fusion and Vaporization for Selected Substances

Substance	ΔH_{fus} (cal/g)	ΔH_{vap} (cal/g)
aluminum (Al)	94.0	2,602
gold (Au)	15.3	409
iron (Fe)	63.2	1,504
water (H_2O)	79.9	540
sodium chloride (NaCl)	123.5	691
ethanol (C_2H_5OH)	45.2	200.3
benzene (C_6H_6)	30.4	94.1

Looking Closer: Sublimation

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \tag{14.6.5}$$

This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At −78.5°C (−109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$CO_2(s) \xrightarrow{-78.5^\circ C} CO_2(g) \tag{14.6.6}$$

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it goes directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Melting Point

Solids are similar to liquids in that both are condensed states, with particles that are far closer together than those of a gas. However, while liquids are fluid, solids are not. The particles of most solids are packed tightly together in an orderly arrangement. The motion of individual atoms, ions, or molecules in a solid is restricted to **vibrational motion** about a fixed point. Solids are almost completely **incompressible** and are the most dense of the three states of matter.

As a solid is heated, its particles vibrate more rapidly as the solid absorbs kinetic energy. Eventually, the organization of the particles within the solid structure begins to break down and the solid starts to melt. The **melting point** is the temperature at which a solid changes into a liquid. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid. As with boiling points, the melting point of a solid is dependent on the strength of those attractive forces. Sodium chloride ($\mathbf{NaCl}$) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at $\mathbf{801°C}$. Ice (solid $\mathbf{H_2O}$) is a molecular compound composed of molecules that are held together by hydrogen bonds. Though hydrogen bonds are the strongest of the intermolecular forces, the strength of hydrogen bonds is much less than that of ionic bonds. The melting point of ice is $\mathbf{0°C}$.

The melting point of a solid is the same as the freezing point of the liquid. At that temperature, the solid and liquid states of the substance are in equilibrium. For water, this equilibrium occurs at $\mathbf{0°C}$.

$$\mathbf{H_2O}\,(s) \rightleftharpoons \mathbf{H_2O}\,(l)$$

We tend to think of solids as those materials that are solid at room temperature. However, all materials have melting points of some sort. Gases become solids at extremely low temperatures, and liquids will also become solid if the temperature is low enough. The table below gives the melting points of some common materials.

Table **14.6.2**: Melting Points of Common Materials

Materials	Melting Point (°C)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961
Pure gold	1063
Iron	1538

? Exercise 14.6.2

a. Explain what happens when heat flows into or out of a substance at its melting point or boiling point.
b. How does the amount of heat required for a phase change relate to the mass of the substance?

Answer a

The energy goes into changing the phase, not the temperature.

Answer b

The amount of heat is a constant per gram of substance.

Summary

- There is an energy change associated with any phase change.
- Sublimation is the change of state from a solid to a gas, without passing through the liquid state.
- Deposition is the change of state from a gas to a solid.
- Carbon dioxide is an example of a material that easily undergoes sublimation.
- The melting point is the temperature at which a solid changes into a liquid.
- Intermolecular forces have a strong influence on melting point.

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14.7: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.*

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we explicitly consider three kinds of intermolecular interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding, and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure **14.7.1*a***.

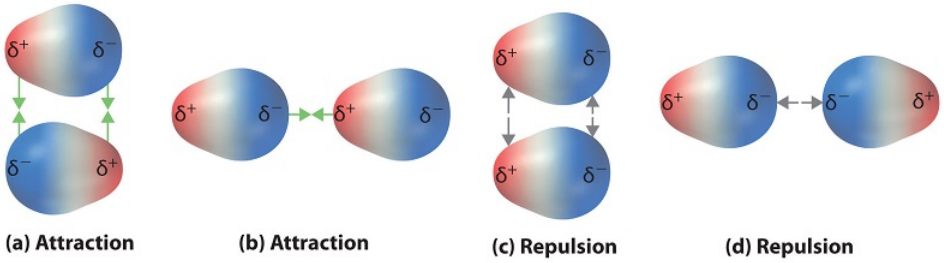


Figure **14.7.1**: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions. (CC BY-SA-NC; anonymous)

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure **14.7.1*c***). Hence dipole–dipole interactions, such as those in Figure **14.7.1*b***, are *attractive intermolecular interactions*, whereas those in Figure **14.7.1*d*** are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure **14.7.2**. On average, however, the attractive interactions dominate.

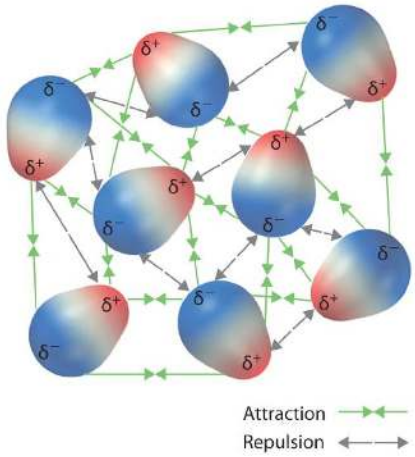


Figure **14.7.2**: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as **HCl**, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, **NaCl**, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table **14.7.1**.

Table **14.7.1**: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

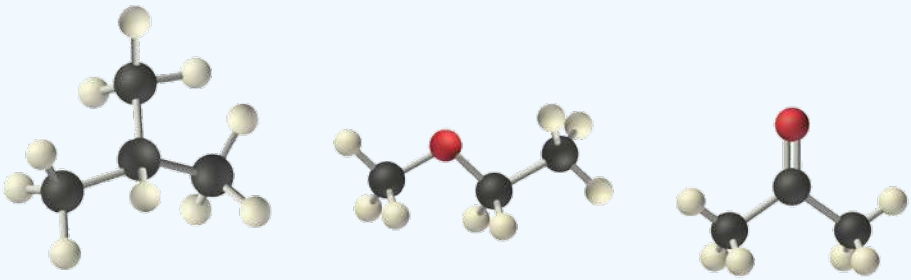
> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*



Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 14.7.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane Ethyl methyl ether Acetone

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 14.7.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table **14.7.2**).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table **14.7.2**: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure **14.7.3**, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

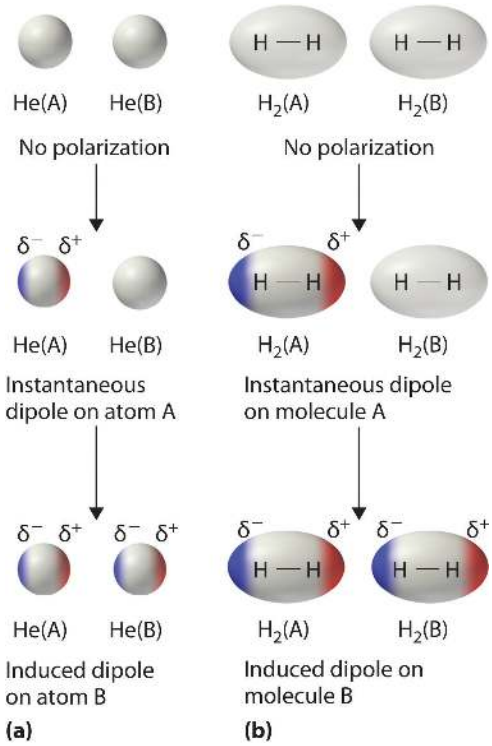


Figure **14.7.3**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure **14.7.3**, tends to become more pronounced as atomic and molecular masses increase (Table **14.7.2**). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure **14.7.4**). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure **14.7.4** shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

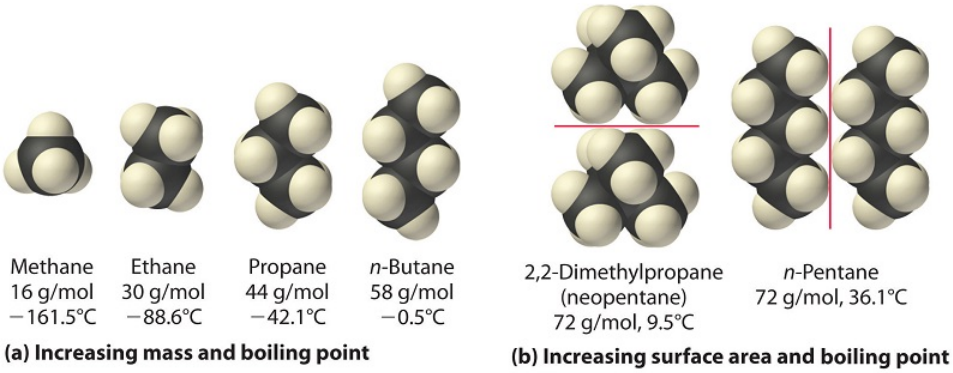


Figure **14.7.4**: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.



Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 14.7.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane

to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 14.7.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure **14.7.5**. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

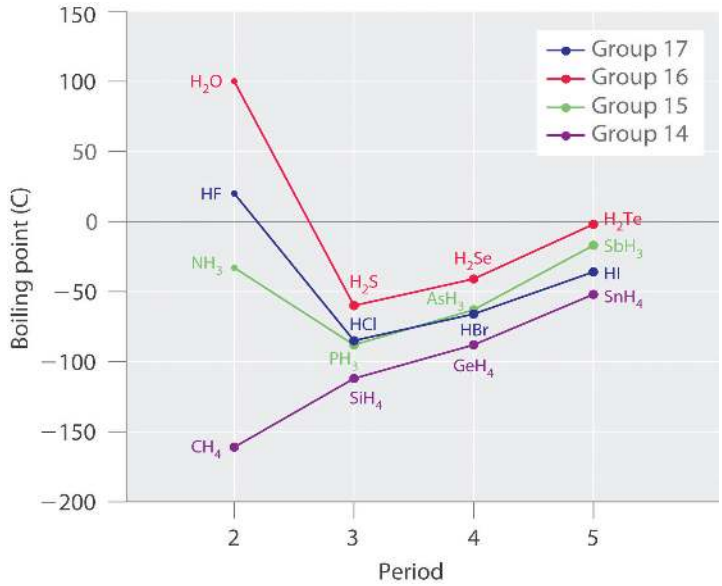


Figure **14.7.5**: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Group 14 is in purple, group 15 is in green, group 16 is red, and group 17 is blue. Graph of boiling point against period.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure **14.7.6**. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms

and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.

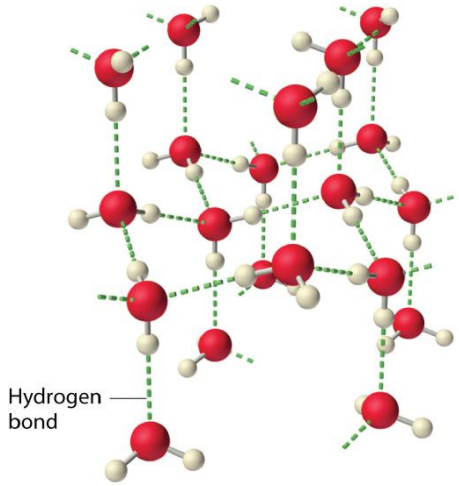


Figure 14.7.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.



Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 14.7.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

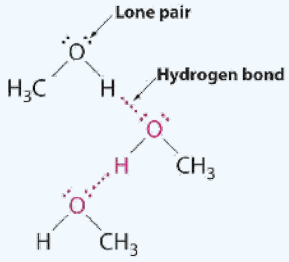
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



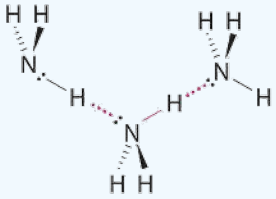
Hydrogen bonding in methanol

Exercise 14.7.3

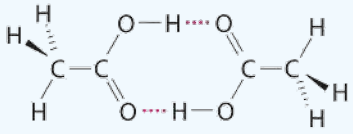
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Hydrogen bonding in ammonia between nitrogen and hydrogen. hydrogen bonding in acetic acid is between oxygen and hydrogen.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen

bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 14.7.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

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

Exercise 14.7.4

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

Answer

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

Example 14.7.5

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 14.7.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. 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. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules; their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage like structure that is less dense than liquid water.

14.7: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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14.8: Cleaning with Soap

Learning Objectives

- Describe the mechanism by which soaps exert their cleansing action.
- List the benefits and problems with using soap.

Personal Cleanliness

Soap is a salt of a fatty acid[1] used in a variety of cleansing and lubricating products. In a domestic setting, soaps are surfactants usually used for washing, bathing, and other types of housekeeping. In industrial settings, soaps are used as thickeners, components of some lubricants, and precursors to catalysts.

When used for cleaning, soap solubilizes particles and grime, which can then be separated from the article being cleaned. In hand washing, as a surfactant, when lathered with a little water, soap kills microorganisms by disorganizing their membrane lipid bilayer and denaturing their proteins. It also emulsifies oils, enabling them to be carried away by running water.[2]

Industrially manufactured **bar soaps** became available in the late 18th century, as advertising campaigns in Europe and America promoted popular awareness of the relationship between cleanliness and health.[35] In modern times, the use of soap has become commonplace in industrialized nations due to a better understanding of the role of hygiene in reducing the population size of pathogenic microorganisms (Figure **14.8.1**).



Figure **14.8.1** Modern Soap Shop in Tubeingen , Germany. Source: Wikipedia

Soap Making: Fat Plus Lye Forms a Soap Plus Glycerol

The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon.[10] A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC.[11]

The Ebers papyrus (Egypt, 1550 BC) indicates the ancient Egyptians bathed regularly and combined animal and vegetable oils with alkaline salts to create a soap-like substance. Egyptian documents mention a similar substance was used in the preparation of wool for weaving.[12]In the reign of Nabonidus (556–539 BC), a recipe for soap consisted of *uhulu* [ashes], cypress [oil] and sesame [seed oil] "for washing the stones for the servant girls".[13]In ancient Israel, the ashes from barilla plants, such as species of Salsola, saltwort (*Seidlitzia rosmarinus*) and *Anabasis*, were used in soap production, known as potash



Figure 14.8.2 Advertising for medicated toilet soap. Source: Wikipedia

Until the Industrial Revolution, soapmaking was conducted on a small scale and the product was rough. In 1780, James Keir established a chemical works at Tipton, for the manufacture of alkali from the sulfates of potash and soda, to which he afterwards added a soap manufactory. William Gossage produced low-priced, good-quality soap from the 1850s. Robert Spear Hudson began manufacturing a soap powder in 1837, initially by grinding the soap with a mortar and pestle. American manufacturer Benjamin T. Babbitt introduced marketing innovations that included sale of bar soap and distribution of product samples. William Hesketh Lever and his brother, James, bought a small soap works in Warrington in 1886 and founded what is still one of the largest soap businesses, formerly called Lever Brothers and now called Unilever. These soap businesses were among the first to employ large-scale advertising campaigns. A poster advertising is shown in Figure 14.8.2.

Liquid soap was not invented until the nineteenth century; in 1865, William Shepphard patented a liquid version of soap.[40] In 1898, B.J. Johnson developed a soap derived from palm and olive oils; his company, the B.J. Johnson Soap Company, introduced "Palmolive" brand soap that same year.[41] This new brand of soap became popular rapidly, and to such a degree that B.J. Johnson Soap Company changed its name to Palmolive.[42]

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called **saponification**. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):

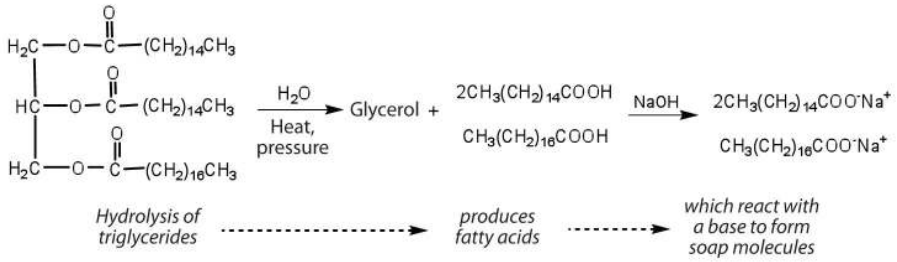


***Figure* 14.8.3** *Saponification.*

How Soap Works

The cleansing action of soap is determined by its polar and non-polar structures in conjunction with an application of solubility principles. The long hydrocarbon chain is of course non-polar and hydrophobic (repelled by water). The "salt" end of the soap molecule is ionic and hydrophilic (water soluble). Examples of soap and detergent molecules, are shown in Figure 14.8.4. The use of such compounds as cleaning agents is facilitated by their surfactant character, which lowers the surface tension of water, allowing it to penetrate and wet a variety of materials.

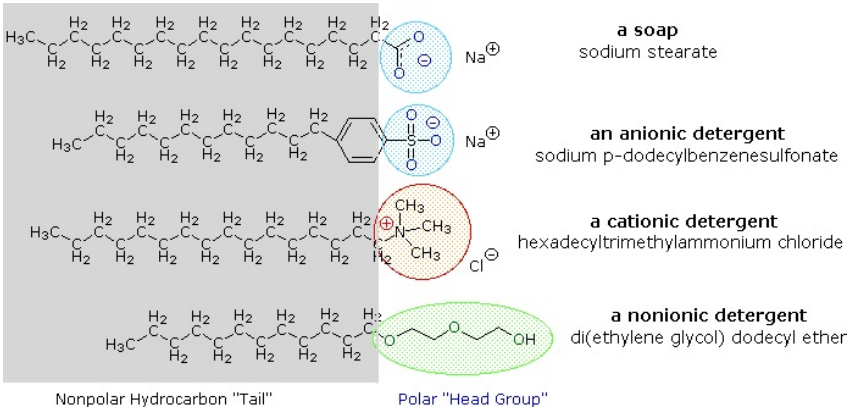


Figure 14.8.4 Soap and detergent molecules with different polar structures.

When soap is added to water, the ionic-salt end of the molecule is attracted to water and dissolved in it. The non-polar hydrocarbon end of the soap molecule is repelled by water. A drop or two of soap in water forms a monolayer (Figure 14.8.5) on the water surface as shown in the graphics on the left. The soap molecules "stand up" on the surface as the polar carboxyl salt end is attracted to the polar water. The non-polar hydrocarbon tails are repelled by the water, which makes them appear to stand up.

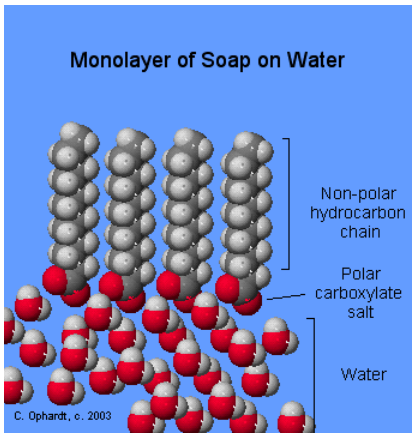


Figure 14.8.5 Monolayer of soap on water.

Soap vs. oil vs. water

Water alone is not able to penetrate grease or oil because they are of opposite polarity. When grease or oil (non-polar hydrocarbons) are mixed with a soap- water solution, the soap molecules work as a "bridge" between polar water molecules and non-polar oil molecules. Soap molecules have both properties of non-polar and polar at opposite ends of the molecule.

The oil is a pure hydrocarbon so it is non-polar. The non-polar hydrocarbon tail of the soap dissolves into the oil. That leaves the polar carboxylate ion of the soap molecules are sticking out of the oil droplets, the surface of each oil droplet is negatively charged. As a result, the oil droplets repel each other and remain suspended in solution (this is called an emulsion) to be washed away by a stream of water. The outside of the droplet is also coated with a layer of water molecules.

The graphic on Figure 14.8.6 although not strictly a representation of the above description is a micelle that works in much the same fashion. The oil would be a the center of the micelle.

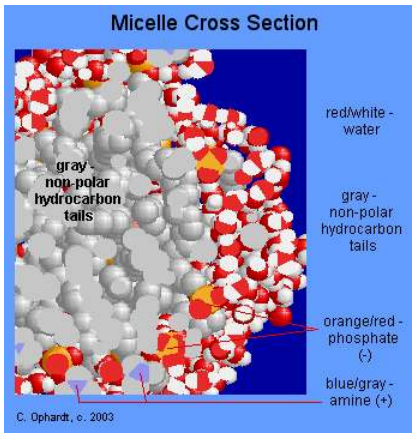


Figure **14.8.6** A micelle with oil at the center.

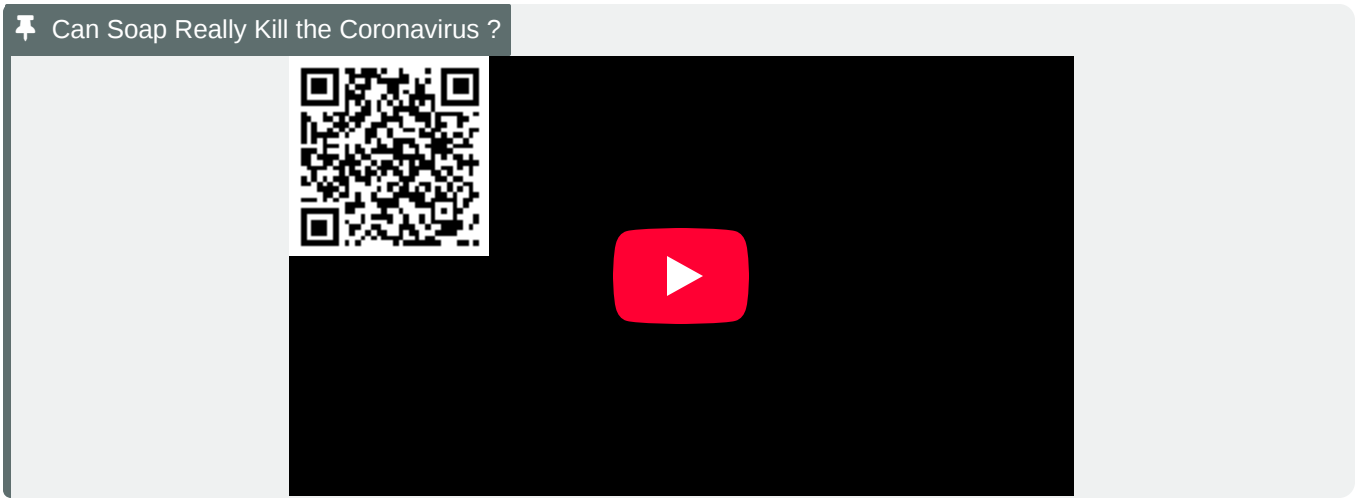
Disadvantages and Advantages of Soap

The importance of soap to human civilization is documented by history, but some problems associated with its use have been recognized. One of these is caused by the weak acidity (pKa ca. 4.9) of the fatty acids. Solutions of alkali metal soaps are slightly alkaline (pH 8 to 9) due to hydrolysis. If the pH of a soap solution is lowered by acidic contaminants, insoluble fatty acids precipitate and form a scum. A second problem is caused by the presence of calcium and magnesium salts in the water supply (hard water). These divalent cations cause aggregation of the micelles, which then deposit as a dirty scum.

In the reaction below, the sodium cation in soap is replaced by calcium to form calcium stearate. The white precipitate, also termed as soap scum could form deposits on surfaces and inside plumbing.

$$2\ C_{17}H_{35}COO^{-}Na^{+} + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca + 2\ Na^{+}$$

Soap is still widely popular product as it is a low cost, readily available product used for personal hygiene and cleanliness. Use of soap doesn't lead to pollution. Soap is biodegradable as it can be broken down by microorganisms found in sewage.



***Video* 14.8.1** *Soap and coronavirus.*

Water Softeners

Water softening is the removal of calcium, magnesium, and certain other metal cations in hard water. The resulting soft water requires less soap for the same cleaning effort, as soap is not wasted bonding with calcium ions. Soft water also extends the lifetime of plumbing by reducing or eliminating scale build-up in pipes and fittings. Water softening is usually achieved using lime softening or ion-exchange resins (see Figure **14.8.7**) but is increasingly being accomplished using nanofiltration or reverse osmosis membranes.

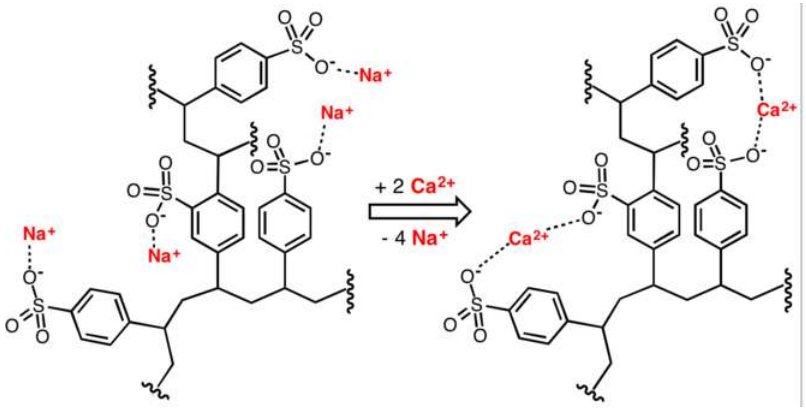


Figure **14.8.7** *Idealized image of water softening process involving replacement of calcium ions in water with sodium ions donated by a cation exchange resin*

How to soften hard water

Some wish to soften hard water to control its irritating, and in many cases damaging, effects. The diminished ability of soap to lather is not only annoying, but can also be potentially harmful economically. Businesses that depend on the foaming of soap, such as car washes and pet groomers, may wish to soften hard water to avoid excessive use of soap due to a decreased ability to lather. Likewise, it is often necessary to soften water that comes into contact with pipes to avoid the destructive and compromising build-up of deposits. Also, many people may find the calcifying effects that hard water has on faucets and other items unfavorable and choose to soften the water to prevent such mineral deposits from forming. Still others may dislike the sticky, dry feeling left by the precipitation of soap scum onto the skin. Whatever the reasons, there are many processes available to soften hard water.

Ion Exchange

One way to soften water is through a process called ion exchange. During ion exchange, the unwanted ions are "exchanged" for more acceptable ions. In many cases, it is desirable to replace the hard water ions, such as Ca^{2+} and Mg^{2+}, with more agreeable ions, like that of Na^{+}. To do this, the hard water is conducted through a zeolite or resin-containing column, which binds the unwanted ions to its surface and releases the more tolerable ions. In this process, the hard water ions become "fixed" ions because of their attachment to the resin material. These fixed ions displace the desirable ions (Na^{+}), now referred to as counterions, from the column, thus exchanging the ions in the water. This process is illustrated in Figure **14.8.8**.

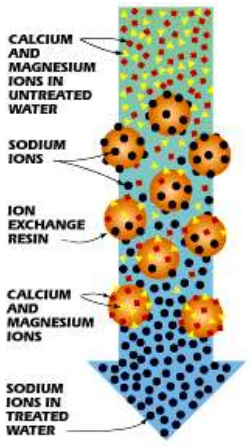


Figure **14.8.8** : Illustration of Ion Exchange.

Unfortunately, this process has the disadvantage of increasing the sodium content of drinking water, which could be potentially hazardous to the health of people with sodium-restricted diets.

Lime Softening

Another process is called lime softening. In this process, the compound calcium hydroxide, $Ca(OH)_2$, is added to the hard water. The calcium hydroxide, or "slaked lime," raises the pH of the water and causes the calcium and magnesium to precipitate into

$CaCO_3$ and $Mg(OH)_2$. These precipitates can then be easily filtered out due to their insolubility in water, shown below by the small solubility constant of magnesium hydroxide (the solubility product constant for calcium carbonate is shown above). After precipitation and removal of the offending ions, acid is added to bring the pH of the water back to normal.

$$Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)} \tag{4a}$$

Chelation

Chelating agents can also be used to soften hard water. Polydentate ligands, such as the popular hexadentate ligand EDTA, bind the undesirable ions in hard water. These ligands are especially helpful in binding the magnesium and calcium cations, which as already mentioned are highly prevalent in hard water solutions. The chelating agent forms a very stable ring complex with the metal cations, which prevents them from interacting with any other substances that may be introduced to the solution, such as soap. In this way, chelators are able to diminish the negative effects associated with hard water. A simplified equation representing the chelation of the metal calcium cation (Ca^{2+}) with the hexadentate ligand EDTA is shown below. The large value of the formation constant (K_f) reflects the tendency of the reaction to proceed to completion in the forward direction.

$$Ca^{2+} + EDTA^{4-} \longrightarrow [Ca(EDTA)]^{2-} \tag{5a}$$

Reverse Osmosis

The final process, reverse osmosis, uses high pressures to force the water through a semipermeable membrane. This membrane is generally intended to be impermeable to anything other than water. The membrane serves to filter out the larger ions and molecules responsible for the water's hardness, resulting in softened water. During this process, the water is forced from an area with a high concentration of solute in the form of dissolved metal ions and similar compounds, to an area that is very low in the concentration of these substances. In other words, the water moves from a state of hardness to a softer composition as the ions causing the water's hardness are prevented passage through the membrane. Reverse Osmosis does have a disadvantage of wasting wastewater compared to other water treatment methods. This process is shown in Figure 14.8.9 below. Note that this figure describes the desalination of salt water. However, the process for softening hard water is the same.

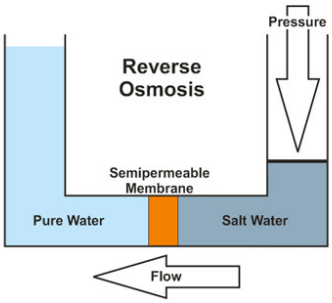


Figure 14.8.9: Depiction of Reverse Osmosis.

Making Hard Water Soft



***Video* 14.8.2** *How to soften hard water.*

Summary

- Soap, as a cleaning agent, solubilizes particles and grime, which can then be easily removed from the article being cleaned.
- In hand washing, soap is an excellent surfactant, that destroys microorganisms by damaging their cellular membranes and denaturing their proteins.
- Soap is an inexpensive, readily available cleaning agent that is also's effectivenes is diminished biodegradable. However, it's effectiveness is diminished when used with hard water.

Contributors

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CHAPTER OVERVIEW

15: Radioactivity and Nuclear Chemistry

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In today's society, the term *radioactivity* conjures up a variety of images:

- Nuclear power plants producing hydrocarbon-free energy, but with potentially deadly by-products that are difficult to store safely.
- Bombs with the capacity to use nuclear reactions that produce devastating explosions with horrible side effects on the earth as we know it, and on the surviving populations that inhabit it.
- Medical technology that utilizes nuclear chemistry to peer inside living things to detect disease, and the power to irradiate tissues to potentially cure these diseases.
- Fusion reactors that hold the promise of limitless energy with few toxic side products.

Radioactivity has a colorful history and clearly presents a variety of social and scientific dilemmas. In this chapter we will introduce the basic concepts of radioactivity, nuclear equations, and the processes involved in nuclear fission and nuclear fusion.

15.1: The Discovery of Radioactivity

15.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

15.3: Detecting Radioactivity

15.4: Natural Radioactivity and Half-Life

15.5: Radiocarbon Dating- Using Radioactivity to Measure the Age of Fossils and Other Artifacts

15.6: The Discovery of Fission and the Atomic Bomb

15.7: Nuclear Power- Using Fission to Generate Electricity

15.8: Nuclear Fusion- The Power of the Sun

15.9: The Effects of Radiation on Life

15.10: Radioactivity in Medicine

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15.1: The Discovery of Radioactivity

Learning Objectives

- List the most common emissions from naturally radioactive nuclei.
- Compare the energy released per gram of matter in nuclear reactions to that in chemical reactions.
- Express the relationship between nuclear stability and the nuclei's binding energy per nucleon ratio.

No one could have known in the 1800's that the discovery of the fascinating science and art form of photography would eventually lead to the splitting of the atom. The basis of photography is the fact that visible light causes certain chemical reactions. If the chemicals are spread thinly on a surface but protected from light by a covering, no reaction occurs. When the covering is removed, however, light acting on the chemicals causes them to darken. With millions of cameras in use today, we do not think of it as a strange phenomenon—but at the time of its discovery, photography was a strange and wonderful thing.

Even stranger was the discovery by Wilhelm Roentgen—that radiation other than visible light could expose photographic film. He found that film wrapped in dark paper would react when x-rays went through the paper and struck the film.



Figure **15.1.1**: Image of Becquerel's photographic plate, which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

When Henri Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather didn't cooperate, and Becquerel had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks, and some of these rocks had not been exposed to sunlight at all. In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becquerel had discovered **radioactivity**.

The Curies and Radium

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

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize and for subsequent work; Marie Cure received a second Nobel Prize in 1911. She is the only person ever to receive two Nobel Prizes in science.

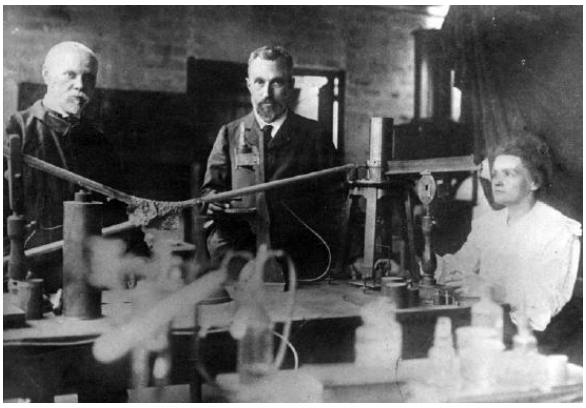


Figure **15.1.2**: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

Further experiments provided information about the characteristics of the penetrating emissions from radioactive substances. It was soon discovered that there were three common types of radioactive emissions. Some of the radiation could pass easily through aluminum foil while some of the radiation was stopped by the foil. Some of the radiation could even pass through foil up to a centimeter thick. The three basic types of radiation were named alpha, beta, and gamma radiation. The actual composition of the three types of radiation was still not known.

Eventually, scientists were able to demonstrate experimentally that the alpha particle, α, was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, β, was a high speed electron, and gamma rays, γ, were a very high energy form of light (even higher energy than x-rays).

Unstable Nuclei May Disintegrate

A nucleus (with one exception, hydrogen-1) consists of some number of protons and neutrons pulled together in an extremely tiny volume. Since protons are positively charged and like charges repel, it is clear that protons cannot remain together in the nucleus unless there is a powerful force holding them there. The force which holds the nucleus together is generated by **nuclear binding energy**.

A nucleus with a large amount of binding energy per nucleon (proton or neutron) will be held together tightly and is referred to as stable. These nuclei do not break apart. When there is too little binding energy per nucleon, the nucleus will be less stable and may disintegrate (come apart). Such disintegration is referred to as **natural radioactivity**. It is also possible for scientists to smash nuclear particles together and cause nuclear reactions between normally stable nuclei. This disintegration is referred to as **artificial radioactivity**. None of the elements above #92 on the periodic table occur on earth naturally—they are all products of artificial (manmade) radioactivity.

When nuclei come apart, they come apart violently accompanied by a tremendous release of energy in the form of heat, light, and radiation. This energy comes from some of the nuclear binding energy. In nuclear changes, the energy involved comes from the nuclear binding energy. However, in chemical reactions, the energy comes from electrons moving energy levels. A typical nuclear change (such as fission) may involve millions of times more energy per atom changing compared to a chemical change (such as burning)!

Summary

- Henri Becquerel, Marie Curie, and Pierre Curie shared the discovery of radioactivity.

Contributions & Attributions

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15.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

Learning Objectives

- Compare qualitatively the ionizing and penetration power of alpha particles (α), beta particles (β), and gamma rays (γ).
- Express the changes in the atomic number and mass number of a radioactive nuclei when an alpha, beta, or gamma particle is emitted.
- Write nuclear equations for alpha and beta decay reactions.

Many nuclei are radioactive; that is, they decompose by emitting particles and in doing so, become a different nucleus. In our studies up to this point, atoms of one element were unable to change into different elements. That is because in all other types of changes discussed, only the electrons were changing. In these changes, the nucleus, which contains the protons that dictate which element an atom is, is changing. All nuclei with 84 or more protons are radioactive, and elements with less than 84 protons have both stable and unstable isotopes. All of these elements can go through nuclear changes and turn into different elements.

In natural radioactive decay, three common emissions occur. When these emissions were originally observed, scientists were unable to identify them as some already known particles and so named them:

- alpha particles (α)
- beta particles (β)
- gamma rays (γ)

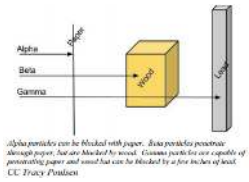
These particles were named using the first three letters of the Greek alphabet. Some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays, except much higher in energy and even more dangerous to living systems.

The Ionizing and Penetration Power of Radiation

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power**. When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation.

Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of a wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous it is. In general, the greater mass present, the greater the ionizing power, and the lower the penetration power.



Alpha particles can be blocked with paper. Beta particles penetrate through paper, but are blocked by wood. Gamma particles are capable of penetrating paper and wood but can be blocked by a few inches of lead. CC Tracy Poulsen

Comparing only the three common types of ionizing radiation, alpha particles have the greatest mass. Alpha particles have approximately four times the mass of a proton or neutron and approximately 8,000 times the mass of a beta particle. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. They collide with molecules very quickly when striking matter, add two electrons, and become a harmless helium atom. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles, but it is only from external sources. In a nuclear explosion or some sort of nuclear accident, where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside of you.

Gamma rays are not particles, but a high energy form of electromagnetic radiation (like x-rays, except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

Table **15.2.1** Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.

Particle	Symbol	Mass	Penetrating Power	Ionizing Power	Shielding
Alpha	α	4amu	Very Low	Very High	Paper Skin
Beta	β	1/2000amu	Intermediate	Intermediate	Aluminum
Gamma	γ	0 (energy only)	Very High	Very Low	2 inches lead

The safest amount of radiation to the human body is zero. It is impossible to completely avoid ionizing radiation, so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure are to limit time of exposure, and to increase distance from the source.

Alpha Decay

The nuclear disintegration process that emits alpha particles is called alpha decay. An example of a nucleus that undergoes alpha decay is uranium-238. The alpha decay of U-238 is

$$^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th} \tag{15.2.1}$$

In this nuclear change, the uranium atom ($^{238}_{92}\text{U}$) transmuted into an atom of thorium ($^{234}_{90}\text{Th}$) and, in the process, gave off an alpha particle. Look at the symbol for the alpha particle: $^{4}_{2}\text{He}$. Where does an alpha particle get this symbol? The bottom number in a nuclear symbol is the number of protons. That means that the alpha particle has two protons in it that were lost by the uranium atom. The two protons also have a charge of $+2$. The top number, 4, is the mass number or the total of the protons and neutrons in the particle. Because it has two protons, and a total of four protons and neutrons, alpha particles must also have two neutrons. Alpha particles always have this same composition: two protons and two neutrons.

Another alpha particle producer is thorium-230.

$$^{230}_{90}\text{Th} \rightarrow {}^{4}_{2}\text{He} + {}^{226}_{88}\text{Ra} \tag{15.2.2}$$

These types of equations are called nuclear equations and are similar to the chemical equivalent discussed through the previous chapters.

Beta Decay

Another common decay process is beta particle emission, or beta decay. A beta particle is simply a high energy electron that is emitted from the nucleus. It may occur to you that we have a logically difficult situation here. Nuclei do not contain electrons and yet during beta decay, an electron is emitted from a nucleus. At the same time that the electron is being ejected from the nucleus, a neutron is becoming a proton. It is tempting to picture this as a neutron breaking into two pieces with the pieces being a proton and an electron. That would be convenient for simplicity, but unfortunately that is not what happens (more on this subject will be explained at the end of this section). For convenience, we will treat beta decay as a neutron splitting into a proton and an electron. The proton stays in the nucleus, increasing the atomic number of the atom by one. The electron is ejected from the nucleus and is the particle of radiation called beta.

To insert an electron into a nuclear equation and have the numbers add up properly, an atomic number and a mass number had to be assigned to an electron. The mass number assigned to an electron is zero (0), which is reasonable since the mass number is the number of protons plus neutrons, and an electron contains no protons and no neutrons. The atomic number assigned to an electron is negative one (-1), because that allows a nuclear equation containing an electron to balance atomic numbers. Therefore, the nuclear symbol representing an electron (beta particle) is

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

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay:

$$ {}^{234}_{90}\text{Th} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{91}\text{Pa} \tag{15.2.3} $$

Gamma Radiation

Frequently, gamma ray production accompanies nuclear reactions of all types. In the alpha decay of U-238, two gamma rays of different energies are emitted in addition to the alpha particle.

$$ {}^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th} + 2{}^{0}_{0}\gamma $$

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown. Nuclear reactions produce a great deal more energy than chemical reactions. Chemical reactions release the difference between the chemical bond energy of the reactants and products, and the energies released have an order of magnitude of $1 \times 10^{3}\ \text{kJ/mol}$. Nuclear reactions release some of the binding energy and may convert tiny amounts of matter into energy. The energy released in a nuclear reaction has an order of magnitude of $1 \times 10^{18}\ \text{kJ/mol}$. That means that nuclear changes involve almost **one million times more energy** per atom than chemical changes!

Note

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown.

The essential features of each reaction are shown in Figure 17.3.2

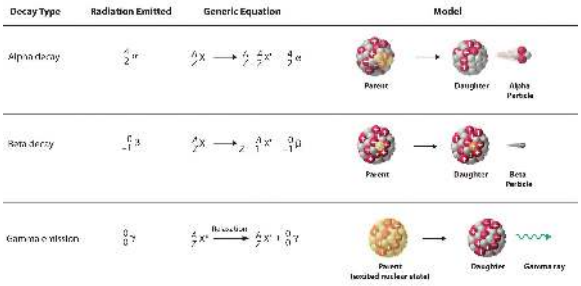


***Figure 17.3.2**: Three most common modes of nuclear decay.*

"Nuclear Accounting"

When writing nuclear equations, there are some general rules that will help you:

- The sum of the mass numbers (top numbers) on the reactant side equal the sum of the mass numbers on the product side.
- The atomic numbers (bottom numbers) on the two sides of the reaction will also be equal.

In the alpha decay of ${}^{238}\text{U}$ (Equation 15.2.1), both atomic and mass numbers are conserved:

- mass number: $238 = 4 + 234$
- atomic number: $92 = 2 + 90$

Confirm that this equation is correctly balanced by adding up the reactants' and products' atomic and mass numbers. Also, note that because this was an alpha reaction, one of the products is the alpha particle, ${}^{4}_{2}\text{He}$.

Note that both the mass numbers and the atomic numbers add up properly for the beta decay of thorium-234 (Equation 15.2.3):

- mass number: $234 = 0 + 234$
- atomic number: $90 = -1 + 91$

The mass numbers of the original nucleus and the new nucleus are the same because a neutron has been lost, but a proton has been gained, and so the sum of protons plus neutrons remains the same. The atomic number in the process has been increased by one since the new nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has become a protactinium-234 nucleus. Protactinium-234 is also a beta emitter and produces uranium-234.

$$ {}^{234}_{91}\text{Pa} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{92}\text{U} \tag{15.2.4} $$

Once again, the atomic number increases by one and the mass number remains the same; this confirms that the equation is correctly balanced.

What About Balancing Charge?

Both alpha and beta particles are charged, but nuclear reactions in Equations 15.2.1, 15.2.3, and most of the other nuclear reactions above, are not balanced with respect to charge, as discussed when balancing redox reactions. When studying nuclear reactions in general, there is typically little information or concern about the chemical state of the radioactive isotopes, because the electrons from the electron cloud are not directly involved in the nuclear reaction (in contrast to chemical reactions).

So it is acceptable to **ignore** charge in balancing nuclear reactions, and concentrate on balancing mass and atomic numbers only.

Example 15.2.1

Complete the following nuclear reaction by filling in the missing particle.

$$ {}^{210}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + ? $$

Solution

This reaction is an alpha decay. We can solve this problem one of two ways:

Solution 1: When an atom gives off an alpha particle, its atomic number drops by 2 and its mass number drops by 4, leaving: ${}^{206}_{84}\text{Po}$. We know the symbol is Po, for polonium, because this is the element with 84 protons on the periodic table.

Solution 2: Remember that the mass numbers on each side must total up to the same amount. The same is true of the atomic numbers.

- Mass numbers: $210 = 4 + ?$
- Atomic numbers: $86 = 2 + ?$

We are left with $^{206}_{84}\text{Po}$.

Example 15.2.2

Write each of the following nuclear reactions.

a) Carbon-14, used in carbon dating, decays by beta emission.

b) Uranium-238 decays by alpha emission.

Solution

a) Beta particles have the symbol $^{0}_{-1}\text{e}$. Emitting a beta particle causes the atomic number to increase by 1 and the mass number to not change. We get atomic numbers and symbols for elements using our periodic table. We are left with the following reaction:

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

b) Alpha particles have the symbol $^{4}_{2}\text{He}$. Emitting an alpha particle causes the atomic number to decrease by 2 and the mass number to decrease by 4. We are left with:

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

Decay Series

The decay of a radioactive nucleus is a move toward becoming stable. Often, a radioactive nucleus cannot reach a stable state through a single decay. In such cases, a series of decays will occur until a stable nucleus is formed. The decay of **U**-238 is an example of this. The **U**-238 decay series starts with **U**-238 and goes through fourteen separate decays to finally reach a stable nucleus, **Pb**-206 (Figure 17.3.3). There are similar decay series for **U**-235 and **Th**-232. The **U**-235 series ends with **Pb**-207 and the **Th**-232 series ends with **Pb**-208.

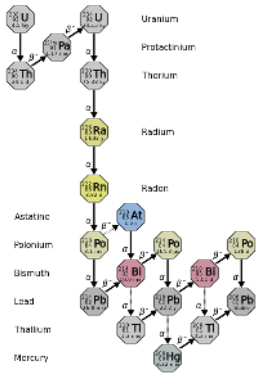


Figure 17.3.3: Uranium-238 decay chain. (CC-BY-3.0 Tosaka)

Several of the radioactive nuclei that are found in nature are present there because they are produced in one of the radioactive decay series. For example, there may have been radon on the earth at the time of its formation, but that original radon would have all decayed by this time. The radon that is present now is present because it was formed in a decay series (mostly by U-238).

Summary

A nuclear reaction is one that changes the structure of the nucleus of an atom. The atomic numbers and mass numbers in a nuclear equation must be balanced. Protons and neutrons are made up of quarks. The two most common modes of natural radioactivity are alpha decay and beta decay. Most nuclear reactions emit energy in the form of gamma rays.

Vocabulary

- **Alpha decay** - A common mode of radioactive decay in which a nucleus emits an alpha particle (a helium-4 nucleus).
- **Beta decay** - A common mode of radioactive decay in which a nucleus emits beta particles. The daughter nucleus will have a higher atomic number than the original nucleus.
- **Quark** - Particles that form one of the two basic constituents of matter. Various species of quarks combine in specific ways to form protons and neutrons, in each case taking exactly three quarks to make the composite particle.

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15.3: Detecting Radioactivity

Learning Objectives

- Understand how the Geiger counter can be used to quantify the rate of ionization radiation.

When alpha, beta or gamma particles collide with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. Alpha, beta and gamma radiation are broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter. A simple schematic of a Geiger counter is shown in Figure 15.3.1.

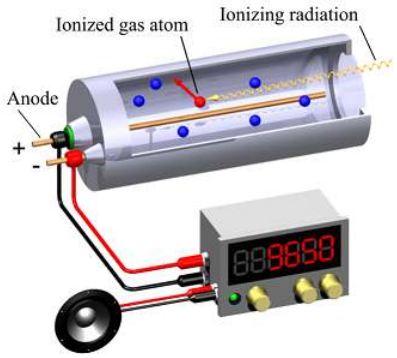


Figure 15.3.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

Although scientists were not aware at the time of the Geiger counter's invention, all of us are subjected to a certain amount of radiation every day. This radiation is called **background radiation** and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These natural sources include:

1. Sources in the earth—including naturally occurring radioactive elements—which are incorporated in building materials, and also in the human body.
2. Sources from space in the form of cosmic rays.
3. Sources in the atmosphere, such as radioactive radon gas released from the earth; and radioactive atoms like carbon-14, produced in the atmosphere by bombardment from high-energy cosmic rays.

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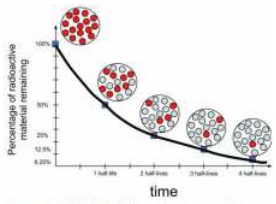
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15.4: Natural Radioactivity and Half-Life

Learning Objectives

- Describe what is meant by the term half-life and what factors affect half-life.
- Calculate the amount of radioactive material that will remain after an integral number of half-lives.
- Find the half-life of an isotope given graphical or other data.
- Describe how carbon-14 is used to determine the age of carbon-containing objects.

Rate of Radioactive Decay



After one half-life, half of the radioactive atoms have decayed. After another half-life, half of the remaining atoms have changed. This pattern continues, with half of the atoms changing over each half-life time.
CC Tracy Poulsen

During natural radioactive decay, not all atoms of an element are instantaneously changed to atoms of another element. The decay process takes time and there is value in being able to express the rate at which a process occurs. A useful concept is **half-life**, which is the time required for half of the starting material to change or decay. Half-lives can be calculated from measurements on the change in mass of a nuclide and the time it takes to occur. The only thing we know is that in the time of that substance's half-life, half of the original nuclei will disintegrate. Although chemical changes are sped up or slowed down by changing factors such as temperature and concentration, these factors have no effect on half-life. Each radioactive isotope will have its own unique half-life that is independent of any of these factors.

The half-lives of many radioactive isotopes have been determined; they have been found to range from extremely long half-lives of 10 billion years, to extremely short half-lives of fractions of a second.

Table 17.5.1: Table of Selected Half-lives

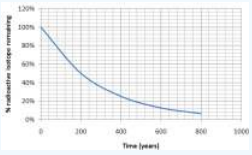
Element	Mass Number (A)	Half-life	Element	Mass Number (A)	Half Life
Uranium	238	4.5 Billion years	Californium	251	800 years
Neptunium	240	1 hour	Nobelium	254	3 seconds
Plutonium	243	5 hours	Carbon	14	5730 years
Americium	245	25 minutes	Carbon	16	740 milliseconds

The quantity of radioactive nuclei at any given time will decrease to half as much in one half-life. For example, if there are $100\ g$ of Cf-251 in a sample at some time, after 800 years, there will be $50\ g$ of Cf-251 remaining; after another 800 years (1600 years total), there will only be $25\ g$ remaining.

Remember, the half-life is the time it takes for half of your sample—no matter how much you have—to remain. Each half-life will follow the same general pattern as Cf-251. The only difference is the length of time it takes for half of a sample to decay.

Example 15.4.3

What is the half-life of an isotope that produces the following graph of decay over time?



Solution

We know that the half-life is the time it takes for half of a sample to change. How long did it take for half of our isotope to change? It took approximately 200 years for 100% of our sample to leave only 50% (half of the original amount) remaining. **The half-life is 200 years.**

*Notice that after another 200 years (400 years total), 25% remains (half of 50%).

Look carefully at the graph in the previous example. All types of radioactive decay make a graph of the same general shape. The only difference is the scale and units of the x-axis, as the half-life time will be different.

Example 15.4.2

If there are 60 grams of Np-240 present, how much Np-240 will remain after 4 hours? (Np-240 has a half-life of 1 hour.)

Solution

We create a table based on Np-240's half-life of 1 hour.

Amount of Np-240 present	Amount of time passed
60 g	0 (this is the amount before any time has passed)
30 g	1 hour (1 half-life)
15 g	2 hours (2 half-lives)
7.5 g	3 hours
3.75 g	4 hours

After 4 hours, only 3.75 g of our original 60 g sample would remain of the radioactive isotope Np-240.

Example 15.4.3

A sample of Ac-225 originally contained 80 grams, and after 50 days only 2.55 grams of the original Ac-225 remain. What is the half life of Ac-225?

Solution

We will tackle this problem similarly to the last problem. The difference is that we are looking for the half-life time. Let's set up a similar table, though:

Amount of Ac-225 present	Amount of time passed
80 g	0
40 g	1 half-life
20 g	2 half-lives
10 g	3 half-lives
5 g	4 half-lives
2.5 g	5 half-lives

We know that 50 days is the same as 5 half-lives. Therefore, 1 half-life is 10 days. The half-life of Ac-225 is 10 days.

Radioactive Dating

An ingenious application of half-life studies established a new science of determining ages of materials by half-life calculations. For geological dating, the decay of U-238 can be used. The half-life of U-238 is 4.5×10^9 years. The end product of the decay of U-238 is Pb-206. After one half-life, a 1.00 gram sample of uranium will have decayed to 0.50 grams of U-238 and 0.43 grams of Pb-206. By comparing the amount of U-238 to the amount of Pb-206 in a sample of uranium mineral, the age of the mineral can be estimated. Present day estimates for the age of the Earth's crust from this method is at 4 billion years.

Organic material (material made from things that were once living, such as paper and fabric) is radioactively dated using the long-lived nuclide of carbon, carbon-14. This method of determining the age of organic material (or once living materials) was given the name radiocarbon dating. The carbon dioxide consumed by living systems contains a certain concentration of $^{14}CO_2$. When an organism dies, the acquisition of carbon-14 stops, but the decay of the C-14 in the body continues. As time goes by, the ratio of C-14 to C-12 decreases at a rate determined by the half-life of C-14. Using half-life equations, the time since the organism died can be calculated. These procedures have been used to determine the age of organic artifacts and determine, for instance, whether art works are real or fake.

Summary and Vocabulary

The half-life of an isotope is used to describe the rate at which the isotope will decay and give off radiation. Using the half-life, it is possible to predict the amount of radioactive material that will remain after a given amount of time. C-14 dating procedures have been used to determine the age of organic artifacts. Its half-life is approximately 5700 years.

- **Background radiation** - Radiation that comes from environmental sources including the earth's crust, the atmosphere, cosmic rays, and radioisotopes. These natural sources of radiation account for the largest amount of radiation received by most people.
- **Half-life** - The time interval required for a quantity of (radioactive) material to decay to half of its original value.

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15.5: Radiocarbon Dating- Using Radioactivity to Measure the Age of Fossils and Other Artifacts

Learning Objectives

- Identify the age of materials that can be approximately determined using Radiocarbon dating.

When we speak of the element Carbon, we most often refer to the most naturally abundant stable isotope ^{12}C. Although ^{12}C is definitely essential to life, its unstable sister isotope ^{14}C has become of extreme importance to the science world. Radiocarbon dating is the process of determining the age of a sample by examining the amount of ^{14}C remaining against its known half-life, 5,730 years. The reason this process works is because when organisms are alive, they are constantly replenishing their ^{14}C supply through respiration, providing them with a constant amount of the isotope. However, when an organism ceases to exist, it no longer takes in carbon from its environment and the unstable ^{14}C isotope begins to decay. From this science, we are able to approximate the date at which the organism lived on Earth. Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

The Carbon-14 Cycle

Radiocarbon dating (usually referred to simply as carbon-14 dating) is a radiometric dating method. It uses the naturally occurring radioisotope carbon-14 (^{14}C) to estimate the age of carbon-bearing materials up to about 58,000 to 62,000 years old. Carbon has two stable, nonradioactive isotopes: carbon-12 (^{12}C) and carbon-13 (^{13}C). There are also trace amounts of the unstable radioisotope carbon-14 (^{14}C) on Earth. Carbon-14 has a relatively short half-life of 5,730 years, meaning that the fraction of carbon-14 in a sample is halved over the course of 5,730 years due to radioactive decay to nitrogen-14. The carbon-14 isotope would vanish from Earth's atmosphere in less than a million years were it not for the constant influx of cosmic rays interacting with molecules of nitrogen (N_2) and single nitrogen atoms (N) in the stratosphere. Both processes of formation and decay of carbon-14 are shown in Figure 1.

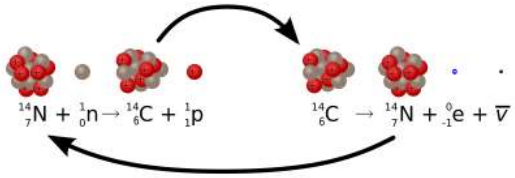


Figure 1: Diagram of the formation of carbon-14 (forward), the decay of carbon-14 (reverse). Carbon-14 is constantly generated in the atmosphere and cycled through the carbon and nitrogen cycles. Once an organism is de-coupled from these cycles (i.e., death), then the carbon-14 decays until there is essentially none left.

When plants fix atmospheric carbon dioxide (CO_2) into organic compounds during photosynthesis, the resulting fraction of the isotope ^{14}C in the plant tissue will match the fraction of the isotope in the atmosphere (and biosphere since they are coupled). After a plant dies, the incorporation of all carbon isotopes, including ^{14}C, stops and the concentration of ^{14}C declines due to the radioactive decay of ^{14}C following.

$$^{14}C \longrightarrow {}^{14}N + e^{-} + \mu_e \tag{15.5.1}$$

This follows first-order kinetics:

$$N_t = N_o e^{-kt} \tag{15.5.2}$$

where

- N_0 is the number of atoms of the isotope in the original sample (at time t = 0, when the organism from which the sample is derived was de-coupled from the biosphere).
- N_t is the number of atoms left after time t.
- k is the rate constant for the radioactive decay.

The half-life of a radioactive isotope (usually denoted by $t_{1/2}$) is a more familiar concept than k for radioactivity, so although Equation 15.5.2 is expressed in terms of k, it is more usual to quote the value of $t_{1/2}$. The currently accepted value for the half-life of ^{14}C is 5,730 years. This means that after 5,730 years, only half of the initial ^{14}C will remain; a quarter will remain after 11,460 years; an eighth after 17,190 years; and so on.

The equation relating rate constant to half-life for first order kinetics is

$$k = \frac{\ln 2}{t_{1/2}} \tag{15.5.3}$$

so the rate constant is then

$$k = \frac{\ln 2}{5.73 \times 10^3} = 1.21 \times 10^{-4} \text{year}^{-1} \tag{15.5.4}$$

and Equation 15.5.1 can be rewritten as

$$N_t = N_o e^{-\ln 2\, t/t_{1/2}} \tag{15.5.5}$$

or

$$t = \left(\frac{\ln \frac{N_o}{N_t}}{\ln 2} \right) t_{1/2} = 8267 \ln \frac{N_o}{N_t} = 19035 \log_{10} \frac{N_o}{N_t} \quad \text{(in years)} \tag{15.5.6}$$

The sample is assumed to have originally had the same $^{14}C/^{12}C$ ratio as the ratio in the atmosphere, and since the size of the sample is known, the total number of atoms in the sample can be calculated, yielding N_0, the number of ^{14}C atoms in the original sample. Measurement of N, the number of ^{14}C atoms currently in the sample, allows the calculation of t, the age of the sample, using the Equation 15.5.6.

Note

Deriving Equation 15.5.6 assumes that the level of ^{14}C in the atmosphere has remained constant over time. However, the level of ^{14}C in the atmosphere has varied significantly, so time estimated by Equation 15.5.6 must be corrected by using data from other sources.

Example 1: Dead Sea Scrolls

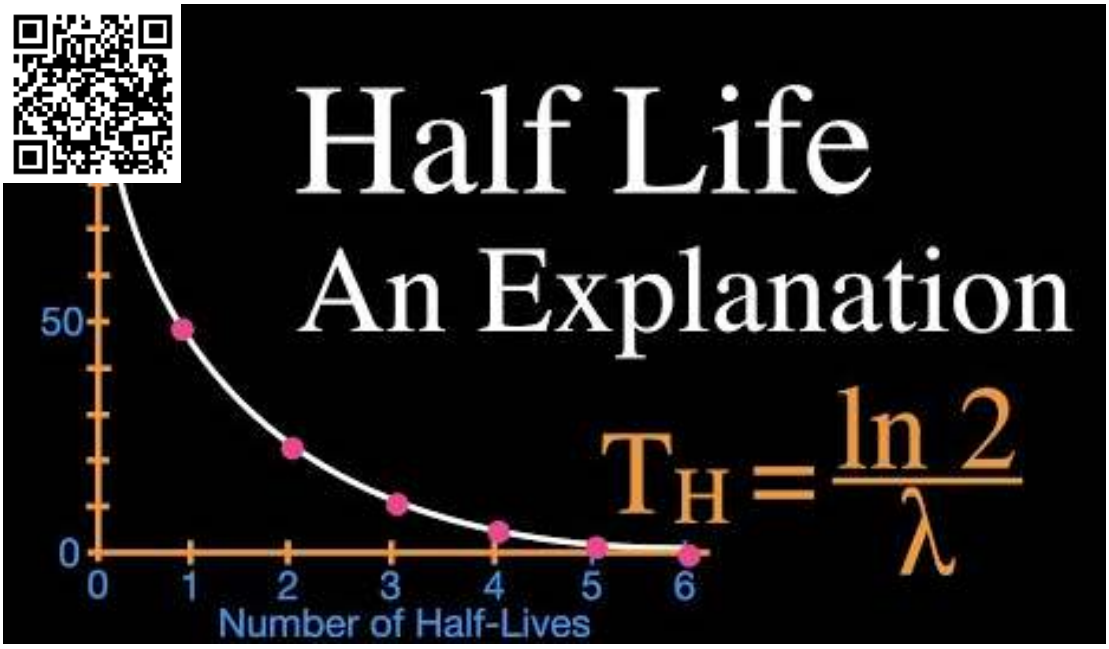
In 1947, samples of the Dead Sea Scrolls were analyzed by carbon dating. It was found that the carbon-14 present had an *activity* (rate of decay) of d/min.g (where d = disintegration). In contrast, living material exhibit an activity of 14 d/min.g. Thus, using Equation 15.5.2,

$$\ln \frac{14}{11} = (1.21 \times 10^{-4})t$$

Thus,

$$t = \frac{\ln 1.272}{1.21 \times 10^{-4}} = 2 \times 10^3 \text{years}$$

From the measurement performed in 1947, the Dead Sea Scrolls were determined to be 2000 years old, giving them a date of 53 BC, and confirming their authenticity. This discovery is in contrast to the carbon dating results for the Turin Shroud that was supposed to have wrapped Jesus' body. Carbon dating has shown that the cloth was made between 1260 and 1390 AD. Thus, the Turin Shroud was made over a thousand years after the death of Jesus.



Describes radioactive half-life and how to do some simple calculations using half-life.

History

The technique of radiocarbon dating was developed by Willard Libby and his colleagues at the University of Chicago in 1949. Emilio Segrè asserted in his autobiography that Enrico Fermi suggested the concept to Libby at a seminar in Chicago that year. Libby estimated that the steady-state radioactivity concentration of exchangeable carbon-14 would be about 14 disintegrations per minute (dpm) per gram. In 1960, Libby was awarded the Nobel Prize in chemistry for this work. He demonstrated the accuracy of radiocarbon dating by accurately estimating the age of wood from a series of samples for which the age was known, including an ancient Egyptian royal barge dating from 1850 BCE. Before Radiocarbon dating was discovered, someone had to find the existence of the ^{14}C isotope. In 1940, Martin Kamen and Sam Ruben at the University of California, Berkeley Radiation Laboratory did just that. They found a form, an isotope, of Carbon that contained 8 neutrons and 6 protons. Using this finding, Willard Libby and his team at the University of Chicago proposed that Carbon-14 was unstable and underwent a total of 14 disintegrations per minute per gram. Using this hypothesis, the initial half-life he determined was 5568, give or take 30 years. The accuracy of this proposal was proven by dating a piece of wood from an Ancient Egyptian barge, the age of which was already known. From that point on, scientists have used these techniques to examine fossils, rocks, and ocean currents; as well as to determine age and event timing. Throughout the years, measurement tools have become more technologically advanced, allowing researchers to be more precise. We now use what is known as the Cambridge half-life of 5730+/- 40 years for Carbon-14. Although it may be seen as outdated, many labs still use Libby's half-life in order to stay consistent in publications and calculations within the laboratory. From the discovery of Carbon-14 to radiocarbon dating of fossils, we can see what an essential role Carbon has played and continues to play in our lives today.

Summary

The entire process of Radiocarbon dating depends on the decay of carbon-14. This process begins when an organism is no longer able to exchange Carbon with its environment. Carbon-14 is first formed when cosmic rays in the atmosphere allow for excess neutrons to be produced, which then react with Nitrogen to produce a constantly replenishing supply of carbon-14 to exchange with organisms.

- Carbon-14 dating can be used to estimate the age of carbon-bearing materials up to about 58,000 to 62,000 years old.
- The carbon-14 isotope would vanish from Earth's atmosphere in less than a million years were it not for the constant influx of cosmic rays interacting with atmospheric nitrogen.
- One of the most frequent uses of radiocarbon dating is to estimate the age of organic remains from archeological sites.

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Problems

1. If, when a hippopotamus lived, there was a total of 25 grams of Carbon-14, how many grams will remain 5730 years after he is laid to rest? 12.5 grams, because one half-life has occurred.
2. How many grams of Carbon-14 will be present in the hippopotamus' remains after three half-lives have passed? 3.125 grams of Carbon-14 will remain after three half-lives.

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15.6: The Discovery of Fission and the Atomic Bomb

Learning Objectives

- Define and give examples of fission and fusion.
- Classify nuclear reactions as fission or fusion.
- List some medical uses of nuclear energy.

Nuclei that are larger than iron-56 may undergo nuclear reactions in which they break up into two or more smaller nuclei. These reactions are called **fission** reactions. Conversely, nuclei that are smaller than iron-56 become larger nuclei in order to be more stable. These nuclei undergo a nuclear reaction in which smaller nuclei join together to form a larger nucleus. Such nuclear reactions are called **fusion** reactions.

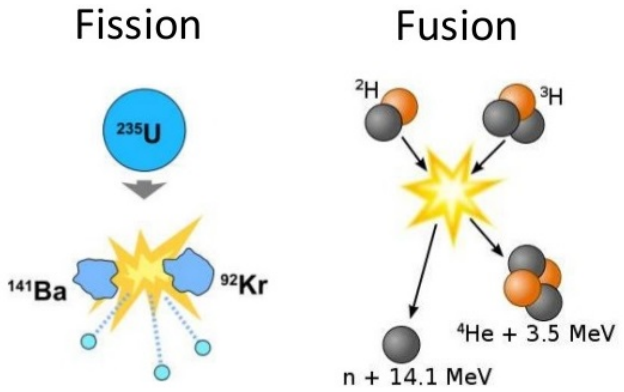


Figure **15.6.1**: (left) Nuclear fission occurs when one large nucleus is split into two or more smaller nuclei. (right) Nuclear fusion happens when two small nuclei combine to make a larger nucleus.

Fission and Chain Reactions

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Nuclear fission was discovered in the late 1930s when U-235 nuclides were bombarded with neutrons and were observed to split into two smaller-mass nuclei.

$$ {}^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} $$

The products shown are only one of many sets of products from the disintegration of a U-235 nucleus. Over 35 different elements have been observed in the fission products of U-235.

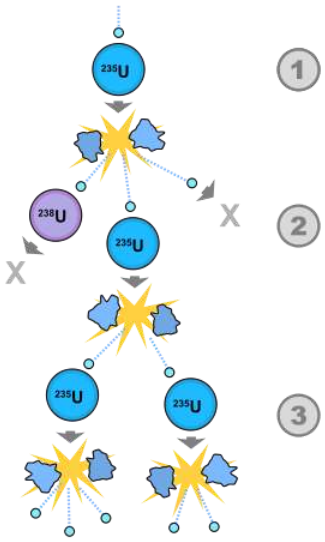


Figure **15.6.2**: A possible nuclear fission chain reaction. 1. A uranium-235 atom absorbs a neutron, and fissions into two new atoms (fission fragments), releasing three new neutrons and a large amount of binding energy. 2. One of those neutrons is absorbed by an atom of uranium-238, and does not continue the reaction. Another neutron leaves the system without being absorbed. However, one neutron does collide with an atom of uranium-235, which then fissions and releases two neutrons and more binding energy. 3. Both of those neutrons collide with uranium-235 atoms, each of which fissions and releases a few neutrons, which can then continue the reaction. (Public Domain.)

When a neutron strikes a **U**-235 nucleus and the nucleus captures a neutron, it undergoes fission, producing two lighter nuclei and three free neutrons. The production of the free neutrons makes it possible to have a self-sustaining fission process—a nuclear **chain reaction**. If at least one of the neutrons goes on to cause another **U**-235 disintegration, the fission will be self-sustaining.

Nuclear Weapons

It is unfortunate that when the topics of radioactivity and nuclear energy come up, most thoughts probably go to weapons of war. The second thought might be about the possibility of nuclear energy contributing to the solution of the energy crisis. Nuclear energy, however, has many applications beyond bombs and the generation of electricity. Radioactivity has huge applications in scientific research, several fields of medicine both in terms of imaging and in terms of treatment, industrial processes, some very useful appliances, and even in agriculture.

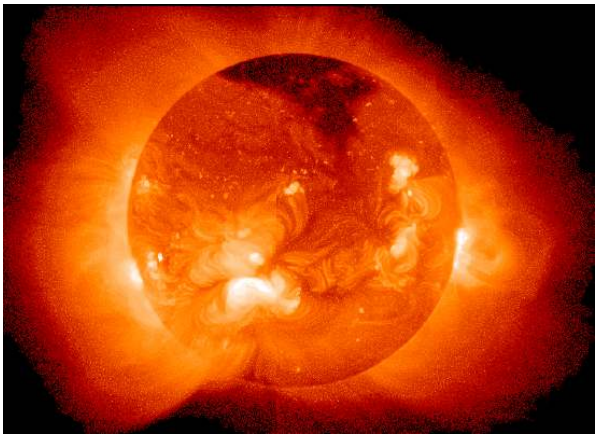


Figure **15.6.3**: The energy that comes from the sun and other stars is produced by fusion. (Public Domain; NASA.)

Summary and Vocabulary

Naturally radioactive elements exist in the earth and are either alpha or beta emitters. Artificial transmutation of elements can be accomplished by bombarding the nuclei of some elements with alpha or subatomic particles. Nuclear radiation also has many medical uses.

- **Chain reaction** - A multi-stage nuclear reaction that sustains itself in a series of fissions, in which the release of neutrons from the splitting of one atom leads to the splitting of others.
- **Critical mass** - The smallest mass of a fissionable material that will sustain a nuclear chain reaction at a constant level.
- **Fission** - A nuclear reaction in which a heavy nucleus splits into two or more smaller fragments, releasing large amounts of energy.
- **Fusion** - A nuclear reaction in which nuclei combine to form more massive nuclei with the simultaneous release of energy.
- **Control rods** - Rods made of chemical elements capable of absorbing many neutrons, that are used to control the rate of a fission chain reaction in a nuclear reactor.

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15.7: Nuclear Power- Using Fission to Generate Electricity

Fission Reactors

Fission reactions can be used in the production of electricity if we control the rate at which the fission occurs. The great majority of all electrical generating systems (whether coal burning power plants, hydroelectric plants, or nuclear power plants) is that they follow a reasonably simple design. The electricity is produced by spinning a coil of wire inside a magnetic field. When a fluid (air, steam, water) is forced through the pipe, it spins the fan blades, which in turn spin the axle. To generate electricity, the axle of a turbine is attached to the loop of wire in a generator. When a fluid is forced through the turbine, the fan blades turn, the turbine axle turns, and the loop of wire inside the generator turns—thus generating electricity.

The essential difference in various kinds of electrical generating systems is the method used to spin the turbine. For a wind generator, the turbine is a windmill. In a geothermal generator, steam from a geyser is forced through the turbine. In hydroelectric generating plants, water falling over a dam passes through the turbine and spins it. In fossil fuel (coal, oil, natural gas) generating plants, the fossil fuel is burned and the heat is used to boil water into steam, and then the steam passes through the turbine to make it spin. In a fission reactor generating plant, a fission reaction is used to boil the water into steam, and the steam passes through the turbine to make it spin. Once the steam is generated by the fission reaction, a nuclear power plant is essentially the same as a fossil fuel plant.

Naturally occurring uranium is composed almost totally of two uranium isotopes. It contains more than 99% uranium-238 and less than 1% uranium-235. It is the uranium-235, however, that is **fissionable** (will undergo fission). In order for uranium to be used as fuel in a fission reactor, the percentage of uranium-235 must be increased, usually to about 3%. (Uranium in which the U-235 content is more than 1% is called **enriched uranium**.)

Once the supply of U-235 is acquired, it is placed in a series of long cylindrical tubes called fuel rods. These fuel cylinders are bundled together with **control rods** made of neutron-absorbing material. The amount of U-235 in all the fuel rods taken together is adequate to carry on a chain reaction, but is less than the critical mass. (In the United States, all public nuclear power plants contain less than a critical mass of U-235 and therefore, could never produce a nuclear explosion.) The amount of heat generated by the chain reaction is controlled by the rate at which the nuclear reaction occurs. The rate of the nuclear reaction is dependent on how many neutrons are emitted by one U-235 nuclear disintegration *and* strike a new U-235 nucleus to cause another disintegration. The purpose of the control rods is to absorb some of the neutrons and thus stop them from causing further disintegration. The control rods can be raised or lowered into the fuel rod bundle. When the control rods are lowered all the way into the fuel rod bundle, they absorb so many neutrons that the chain reaction essentially stops. When more heat is desired, the control rods are raised so that they catch fewer neutrons, the chain reaction speeds up, and more heat is generated. The control rods are operated in a fail-safe system, so that power is necessary to hold them up; during a power failure, gravity will pull the control rods down into the shut off position.

U-235 nuclei can capture neutrons and disintegrate more efficiently if the neutrons are moving slower than the speed at which they are released. Fission reactors use a moderator surrounding the fuel rods to slow down the neutrons. Water is not only a good coolant, but also a good moderator. A common type of fission reactor has the fuel core submerged in a huge pool of water.

You can follow the operation of an electricity-generating fission reactor in the figure below. The reactor core is submerged in a pool of water. The heat from the fission reaction heats the water and the water is pumped into a heat exchanger container where the heated water boils the water in the heat exchanger. The steam from there is forced through a turbine which spins a generator and produces electricity. After the water passes through the turbine, it is condensed back to liquid water and pumped back to the heat exchanger.

In the United States, heavy opposition to the use of nuclear energy was mounted in the late 1960's and early 1970's. Every environmentalist organization in the US opposed the use of nuclear energy; the constant pressure from environmentalist groups caused an increase of public fear and, therefore, opposition to nuclear energy. This is not true today; at least one environmental leader has published a paper in favor of nuclear-powered electricity generation.

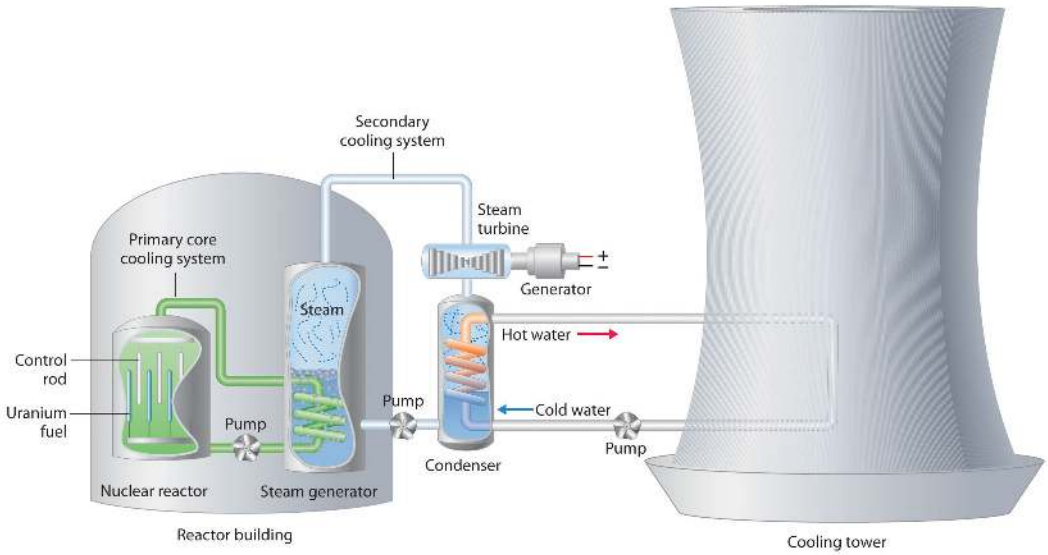


Figure **15.7.1**: A Light-Water Nuclear Fission Reactor for the Production of Electric Power. The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium—which are very effective at absorbing neutrons—are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

In 1979, a reactor core meltdown at Pennsylvania's Three Mile Island nuclear power plant reminded the entire country of the dangers of nuclear radiation. The concrete containment structure (six feet thick walls of reinforced concrete), however, did what it was designed to do—prevent radiation from escaping into the environment. Although the reactor was shut down for years, there were no injuries or deaths among nuclear workers or nearby residents. Three Mile Island was the only serious accident in the entire history of 103 civilian power plants operating for 40 years in the United States. There has never been a single injury or death due to radiation in any public nuclear power plant in the U.S. The accident at Three Mile Island did, however, frighten the public so that there has not been a nuclear power plant built in the U.S. since the accident.

The 103 nuclear power plants operating in the U.S. deliver approximately 19.4% of American electricity with zero greenhouse gas emission. There are 600 coal-burning electric plants in the US delivering 48.5% of American electricity and producing 2 billion tons of CO_2 annually, accounting for 40% of U.S. CO_2 emissions and 10% of global emissions. These coal burning plants also produce 64% of the sulfur dioxide emissions, 26% of the nitrous oxide emissions, and 33% of mercury emissions.

Fusion

Nuclear reactions, in which two or more lighter-mass nuclei join together to form a single nucleus, are called **fusion** reactions or nuclear fusions. Of particular interest are fusion reactions in which hydrogen nuclei combine to form helium. Hydrogen nuclei are positively charged and repel each other. The closer the particles come, the greater the force of repulsion. In order for fusion reactions to occur, the hydrogen nuclei must have extremely high kinetic energies, so that the velocities can overcome the forces of repulsion. These kinetic energies only occur at extreme temperatures such as those that occur in the cores of the sun and other stars. Nuclear fusion is the power source for the stars, where the necessary temperature to ignite the fusion reaction is provided by massive gravitational pressure. In stars more massive than our sun, fusion reactions involving carbon and nitrogen are possible. These reactions produce more energy than hydrogen fusion reactions.

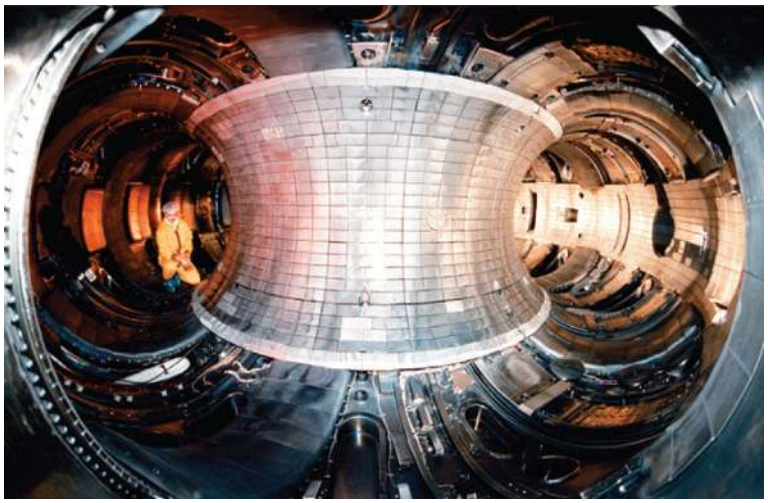


Figure 15.7.2: A Possible Design for a Nuclear Fusion Reactor. The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. Because plasma is essentially a gas composed of ionized particles, it can be confined using a strong magnetic field shaped like a torus (a hollow donut).

Intensive research is now being conducted to develop fusion reactors for electricity generation. The two major problems slowing the development are: finding a practical means for generating the intense temperature needed, and developing a container that will not melt under the conditions of a fusion reaction. Electricity-producing fusion reactors are still a distant dream.

Summary

- Nuclear fission refers to the splitting of atomic nuclei.
- Nuclear fusion refers to the joining together of two or more smaller nuclei to form a single nucleus.
- The fission of U-235 or Pu-239 is used in nuclear reactors.

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15.8: Nuclear Fusion- The Power of the Sun

In addition to fission, a second possible method for obtaining energy from nuclear reactions lies in the fusing together of two light nuclei to form a heavier nucleus. As we see when discussing Figure 1 from Mass-Energy Relationships, such a process results in nucleons which are more firmly bonded to each other, and hence lower in potential energy. This is particularly true if $^{4}_{2}\mathrm{He}$ is formed, because this nucleus is very stable. Such a reaction occurs between the nuclei of the two heavy isotopes of hydrogen, deuterium and tritium:

$$^{2}_{1}\mathrm{D} + {}^{3}_{1}\mathrm{T} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n \tag{15.8.1}$$

For this reaction, $\Delta m = -0.018\ 88$ g mol^{-1} so that $\Delta H_m = -1700$ GJ mol^{-1}. Although very large quantities of energy are released by a reaction like Equation 15.8.1, such a reaction is very difficult to achieve in practice. This is because of the very high activation energy, about 30 GJ mol^{-1}, which must be overcome to bring the nuclei close enough to fuse together. This barrier is created by coulombic repulsion between the positively charged nuclei. The only place where scientists have succeeded in producing fusion reactions on a large scale is in a **hydrogen bomb**. Here, the necessary activation energy is achieved by exploding a fission bomb to heat the reactants to a temperature of about 10^8 K. Attempts to carry out fusion in a more controlled way have met only limited success. At the very high temperatures required, all molecules dissociate and most atoms ionize. A new state of matter called a **plasma** is formed. It is neither solid, liquid, nor gas. Plasma behaves much like the universal solvent of the alchemists by converting any solid material that it contacts into vapor.

Two techniques for producing a controlled fusion reaction are currently being explored. The first is to restrict the plasma by means of a strong magnetic field, rather than the walls of a container. This has met some success, but has not yet been able to contain a plasma long enough for usable energy to be obtained. The second technique involves the sudden compression and heating of pellets of deuterium and tritium by means of a sharply focused laser beam. Again, only limited success has been obtained.

Though these attempts at a controlled fusion reaction have so far been only partially successful, they are nevertheless worth pursuing. Because of the much readier availability of lighter isotopes necessary for fusion, as opposed to the much rarer heavier isotopes required for fission, controlled nuclear fusion would offer the human race an essentially limitless supply of energy. There would still be some environmental difficulties with the production of isotopes such as tritium, but these would be nowhere near the seriousness of the problem caused by the production of the witches brew of radioactive isotopes in a fission reactor. It must be confessed, though, that at the present rate of progress, the prospect of limitless clean energy from fusion seems unlikely in the next decade or two.

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15.9: The Effects of Radiation on Life

Learning Objectives

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure **15.9.1**).

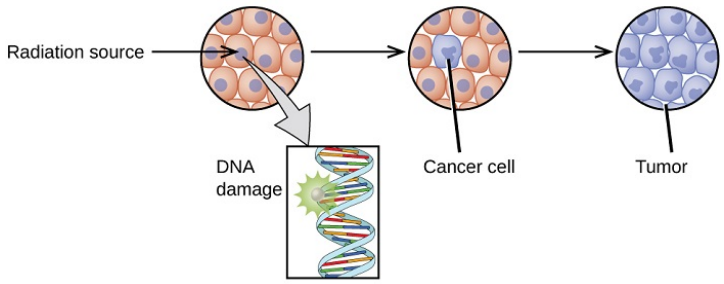


Figure **15.9.1**: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure **15.9.2**).

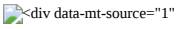


Figure **15.9.2**: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

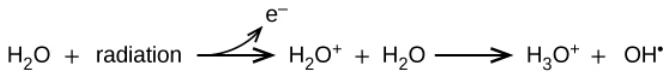


Figure 15.9.3.

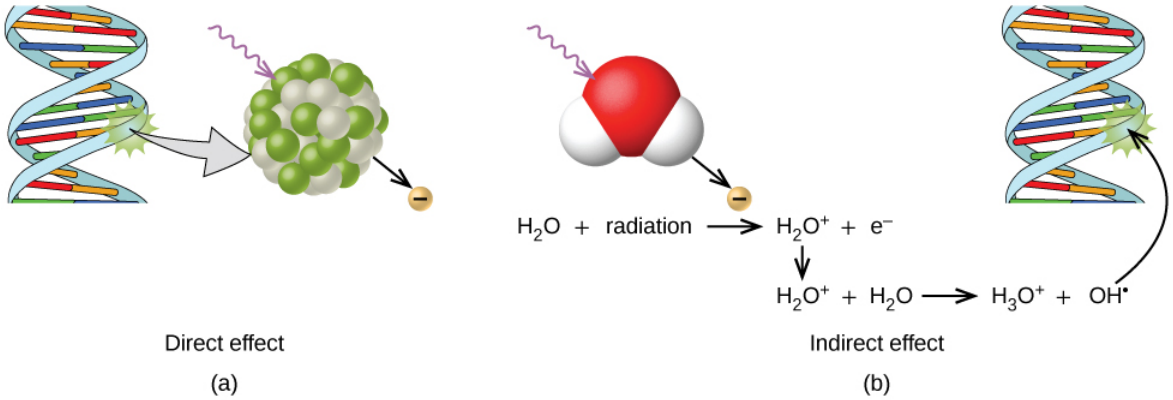


Figure 15.9.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 15.9.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

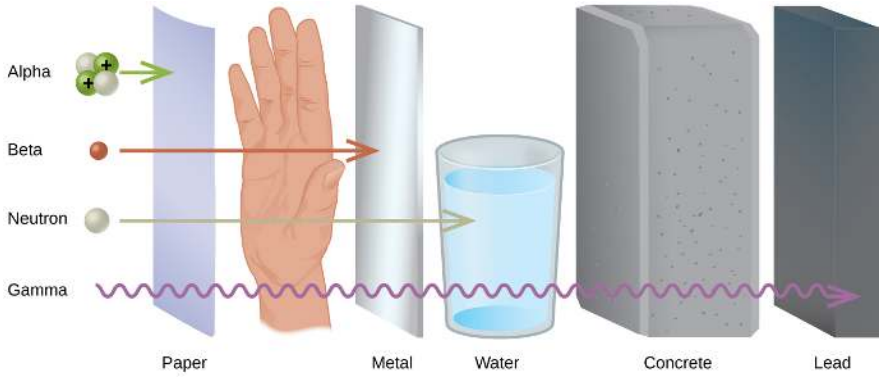


Figure **15.9.4**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person's hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled "Alpha." A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled "Beta" and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled "Neutron" and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, "Paper," "Metal," "Water," "Concrete" and "Lead."

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure **15.9.5**).

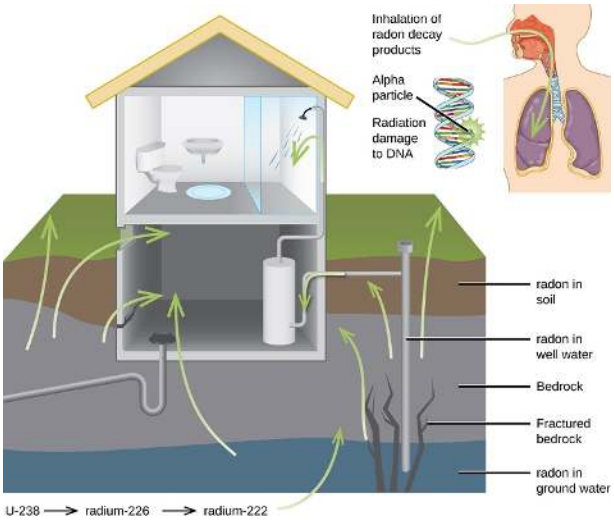


Figure **15.9.5**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of

getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure **15.9.6**). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.



Figure **15.9.6**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

Three photographs are shown and labeled "a," "b" and "c." Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person's hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table **15.9.1**). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = $\mathbf{3.7 \times 10^{10}}$ disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table **15.9.1**: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes $\mathbf{3.7 \times 10^{10}}$ **decays/second**
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor

referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{15.9.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

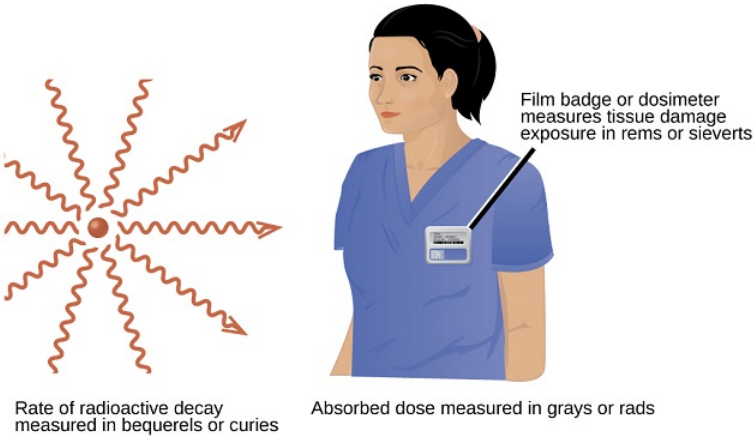


Figure 15.9.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled “Rate of radioactive decay measured in becquerels or curies,” shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads “Film badge or dosimeter measures tissue damage exposure in rems or sieverts” while a phrase under this image states “Absorbed dose measured in grays or rads.”

Example 15.9.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

? Exercise 15.9.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer a

3.56×10^{11} Bq

Answer b

0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 15.9.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

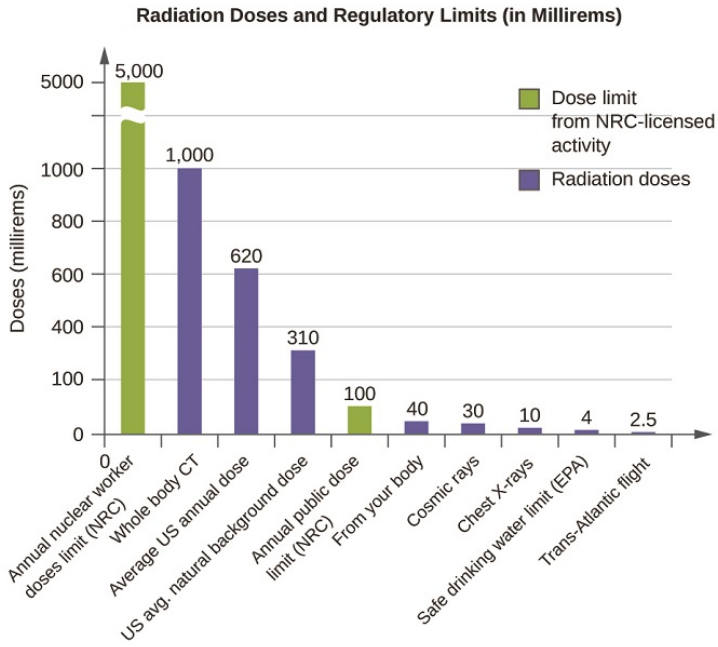


Figure 15.9.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled “Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis” is shown. The y-axis is labeled “Doses in Millirems” and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled “Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis.” The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled “Whole Body C T” while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled “Average U period S period Annual Dose.” The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled “U period S period Natural Background Dose” while the fifth bar, measured to 100 on the y-axis and drawn in red reads “Annual Public Dose Limit, open parenthesis, N R C, close parenthesis.” The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled “From Your Body” while the seventh bar, measured to 30 on the y-axis and drawn in blue reads “Cosmic rays.” The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled “Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis” while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads “Trans Atlantic Flight.” A legend on the graph shows that red means “Dose Limit From N R C dash licensed activity” while blue means “Radiation Doses.”

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table **15.9.2**.

Table **15.9.2**: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)
SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

curie (Ci)
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

Geiger counter
Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

gray (Gy)
SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

ionizing radiation
Radiation that can cause a molecule to lose an electron and form an ion.

millicurie (mCi)
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

nonionizing radiation
Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

radiation absorbed dose (rad)
SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

radiation dosimeter
Device that measures ionizing radiation and is used to determine personal radiation exposure.

relative biological effectiveness (RBE)
Measure of the relative damage done by radiation.

roentgen equivalent man (rem)
Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

scintillation counter
Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

sievert (Sv)
SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

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15.10: Radioactivity in Medicine

Learning Objectives

- Outline manifestations of nuclear medicine.

The field of nuclear medicine has expanded greatly in the last twenty years, particularly in the area of imaging. This section will focus on nuclear medicine involving the types of nuclear radiation introduced in this chapter. The x-ray imaging systems will not be covered.

Radioiodine $(\mathbf{I-131})$ Therapy involves imaging and treatment of the thyroid gland. The thyroid gland is a gland in the neck that produces two hormones that regulate metabolism. In some individuals, this gland becomes overactive and produces too much of these hormones. The treatment for this problem uses radioactive iodine $(\mathbf{I-131})$, which is produced for this purpose in research fission reactors, or by neutron bombardment of other nuclei.

The thyroid gland uses iodine in the process of its normal function. Any iodine in food that enters the bloodstream is usually removed by, and concentrated in, the thyroid gland. When a patient suffering from an overactive thyroid swallows a small pill containing radioactive iodine, the **I**-131 is absorbed into the bloodstream just like non-radioactive iodine, and follows the same process to be concentrated in the thyroid. The concentrated emissions of nuclear radiation in the thyroid destroy some of the gland's cells and control the problem of the overactive thyroid.

Smaller doses of **I**-131 (too small to kill cells) are also used for purposes of imaging the thyroid. Once the iodine is concentrated in the thyroid, the patient lays down on a sheet of film and the radiation from the **I**-131 makes a picture of the thyroid on the film. The half-life of iodine-131 is approximately 8 days so after a few weeks, virtually all of the radioactive iodine is out of the patient's system. During that time, the patient is advised that they will set off radiation detectors in airports and will need to get special permission to fly on commercial flights.

Positron Emission Tomography or PET scan is a type of nuclear medicine imaging. Depending on the area of the body being imaged, a radioactive isotope is either injected into a vein, swallowed by mouth, or inhaled as a gas. When the radioisotope is collected in the appropriate area of the body, the gamma ray emissions are detected by a PET scanner (often called a gamma camera) which works together with a computer to generate special pictures, providing details on both the structure and function of various organs. PET scans are used to:

- Detect cancer.
- Determine the amount of cancer spread.
- Assess the effectiveness of treatment plans.
- Determine blood flow to the heart muscle.
- Determine the effects of a heart attack.
- Evaluate brain abnormalities, such as tumors and memory disorders.
- Map brain and heart function.

External Beam Therapy (EBT) is a method of delivering a high energy beam of radiation to the precise location of a patient's tumor. These beams can destroy cancer cells and, with careful planning, will not kill surrounding cells. The concept is to have several beams of radiation, each of which is sub-lethal, enter the body from different directions. The only place in the body where the beam would be lethal is at the point where all the beams intersect. Before the EBT process, the patient is three-dimensionally mapped using CT scans and x-rays. The patient receives small tattoos to allow the therapist to line up the beams exactly. Alignment lasers are used to precisely locate the target. The radiation beam is usually generated with a linear accelerator. EBT is used to treat the following diseases, as well as others:

- Breast cancer
- Colorectal cancer
- Head and neck cancer
- Lung cancer
- Prostate cancer

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CHAPTER OVERVIEW

16: Solutions

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Solutions play a very important role in many biological, laboratory, and industrial applications of chemistry. Of particular importance are solutions involving substances dissolved in water, or aqueous solutions. Solutions represent equilibrium systems, and the lessons learned in the last chapter will be of particular importance again. Quantitative measurements of solutions are another key component of this chapter. Solutions can involve all physical states—gases dissolved in gases (the air around us), solids dissolved in solids (metal alloys), and liquids dissolved in solids (amalgams—liquid mercury dissolved in another metal such as silver, tin or copper). This chapter is almost exclusively concerned with aqueous solutions, substances dissolved in water.

16.1: Water - Some Unique Properties

16.2: Solutions - Homogeneous Mixtures

16.3: The Dissolution Process

16.4: Solutions of Solids Dissolved in Water- How to Make Rock Candy

16.5: Solutions of Gases in Water

16.6: Solution Concentration- Mass Percent

16.7: Solution Concentration- Molarity

16.8: Solution Dilution

16.9: Freezing Point Depression and Boiling Point Elevation

16.10: Osmosis and Diffusion

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16.1: Water - Some Unique Properties

LEARNING OBJECTIVE

Describe the different properties of water as it relates to its polarity and ability to form hydrogen bonds.

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water. Water is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms (Figure **16.1.1**). Because of the higher electronegativity of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom requires a partial negative charge ($\delta-$), while the hydrogen atoms each acquire a partial positive charge ($\delta+$). The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The $\mathrm{H-O-H}$ bond angle is about $105°$, slightly smaller than the ideal $109.5°$ of an sp^3 hybridized atomic orbital.The bent shape of the water molecule is critical because the polar $\mathrm{O-H}$ bonds do not cancel one another and the molecule as a whole is polar.

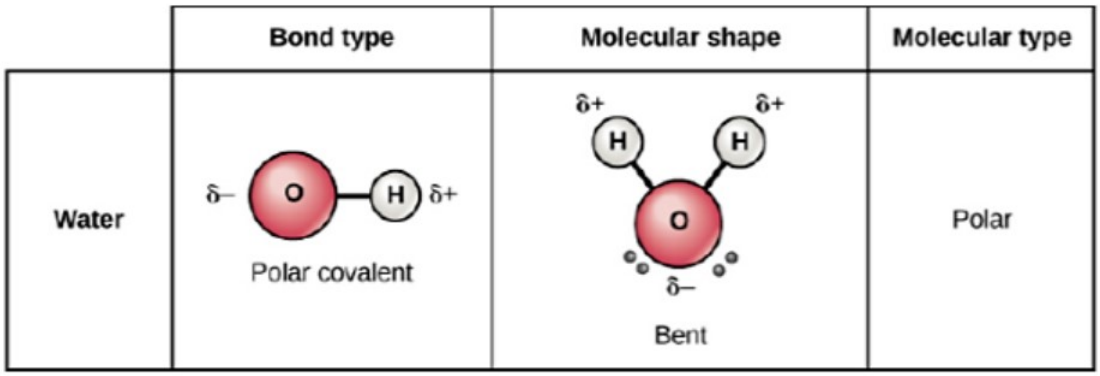


Figure **16.1.1** *Polarity of the water molecule due to the uneven distribution of electrons in its covalent bond. C (From OpenStax Concepts of Biology text)*

Hydrogen Bonds

Due to water's polarity, each water molecule attracts other water molecules as oppositely charged ends of the molecules attract each other. When this happens, a weak interaction occurs between the *positive* hydrogen end from one molecule and the *negative oxygen* end of another molecule. This interaction is called a **hydrogen bond**. This hydrogen bonding contributes to the following water's unique properties.

1. Water is the universal solvent
2. Exists in nature as a solid, liquid, and gas
3. The density of ice is less than liquid water
4. Water has a high heat capacity
5. Water has a high heat of vaporization
6. Water exists as a liquid at room temperature It is important to note here that even we are only focusing on water in this text book, hydrogen bonding also occurs in other substances that have polar molecules.

Density of Water

Liquid water is a fluid. The hydrogen bonds in liquid water constantly break and reform as the water molecules tumble past one another. As water cools, its molecular motion slows and the molecules move gradually closer to one another. The **density** of any

liquid increases as its temperature decreases. For most liquids, this continues as the liquid freezes and the solid state is denser than the liquid state. However, water behaves differently (Table **16.1.1**) . It actually reaches its highest density at about **4°C**.

Table **16.1.1** *Density of Water and Ice*

Temperature (°C)	Density $\left(g/cm^3\right)$
100 (liquid)	0.9584
50	0.9881
25	0.9971
10	0.9997
4	1.0000
0 (liquid)	0.9998
0 (solid)	0.9168

Between **4°C** and **0°C**, the density gradually decreases as the hydrogen bonds begin to form a network characterized by a generally **hexagonal** structure with open spaces in the middle of the hexagons (Figure **16.1.2**).

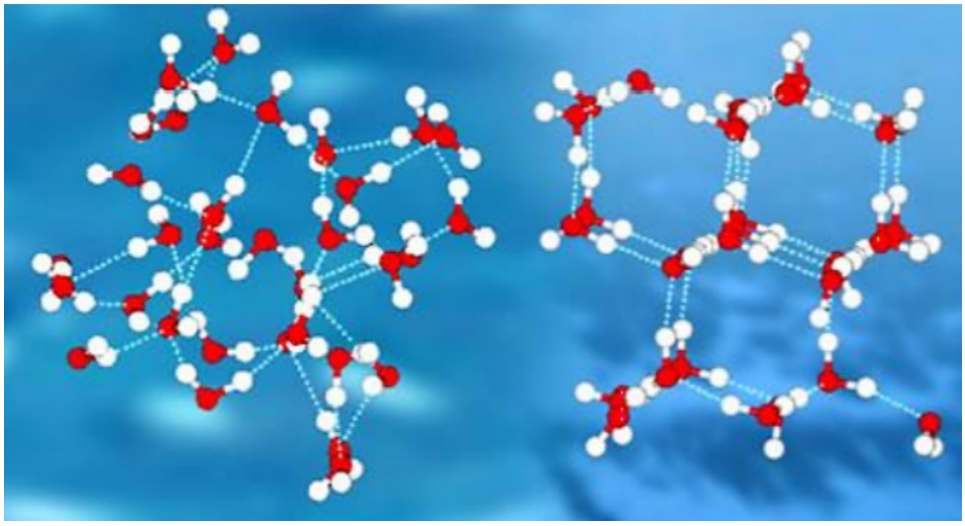


Figure **16.1.2** *Hydrogen bonding makes ice less dense than liquid water. The lattice structure water is more condensed (left structure) than that of ice (right structure). The lattice structure of ice makes it less dense than freely flowing molecules of liquid water, enabling ice to float on liquid water. (Image credit: Lynn Yarris, http://www2.lbl.gov/Science-Articles...ter-solid.html)*

Ice is less dense than liquid water and so it floats. Ponds or lakes begin to freeze at the surface, closer to the cold air. A layer of ice forms, but does not sink as it would if water did not have this unique structure dictated by its shape, polarity, and hydrogen bonding. If the ice were to sink as it froze, entire lakes would freeze solid. Since the ice does not sink, liquid water remains under the ice all winter long. This is important, as fish and other organisms are capable of surviving through winter. Ice is one of only a very few solids that is less dense than its liquid form.

Solvation Ability of Water

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively

charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see Figure **16.1.3**) .

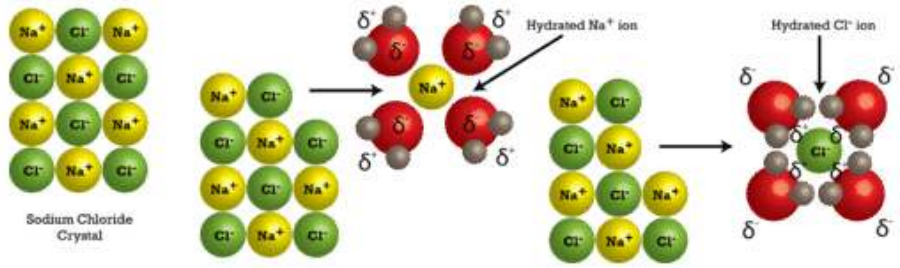


Figure **16.1.3** *The dissolving of sodium chloride in water.*

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual $\mathbf{Na^+}$ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose ($\mathbf{C_{12}H_{22}O_{11}}$) and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecules contain many $\mathbf{-OH}$ groups that can form hydrogen bonds with the water molecules, helping form the sucrose solution.

The Amphoteric Nature of Water

Water is amphoteric: it has the ability to act as either an acid or a base in chemical reactions. According to the Brønsted-Lowry definition, an acid is a proton (H^+) donor and a base is a proton acceptor. When reacting with a stronger acid, water acts as a base; when reacting with a stronger base, it acts as an acid. For instance, water receives an H^+ ion from HCl when hydrochloric acid is formed:

$$HCl(acid) + H_2O(base) \rightleftharpoons H_3O^+ + Cl^-$$

In the reaction with ammonia, NH_3, water donates a H^+ ion, and is thus acting as an acid:

$$NH_3(base) + H_2O(acid) \rightleftharpoons NH^+_4 + OH^-$$

High Heat Capacity and Specific Heat of Water

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. Table **16.1.2** list specific heats of various substances compared to water.Water has the highest **specific heat capacity** of any liquid. Water's high heat capacity is a property caused by hydrogen bonding among the water molecules. **Specific heat** is defined as the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius. For water, this amount is **1 cal/g°C**. The units for specific heat can either be in the SI units of joules per gram per degree ($\mathbf{J/g°C}$) or calories per gram per degree ($\mathbf{cal/g°C}$). This text will use $\mathbf{J/g°C}$ for specific heat.



Figure **16.1.4** *This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.*

It takes water a long time to heat up and a long time to cool down. In fact, the specific heat capacity of water is about five times more than that of sand. This explains why land cools faster than the sea. Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days. Water is used as a coolant for machinery because it is able to absorb large quantities of heat (Figure **16.1.4**). Due to its high heat capacity, warm-blooded animals use water to disperse heat more evenly and maintain temperature in their bodies: it acts in a similar manner to a car's cooling system, transporting heat from warm places to cool places, causing the body to maintain a more even temperature.

Table **16.1.2** *Specific Heats of Some Common Substances*

Substance	Specific Heat $(J/g^{\circ}C)$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

High Heat of Vaporization of Water

Water in its liquid form has an unusually high boiling point temperature, a value close to 100°C. As a result of the network of hydrogen bonding present between water molecules, a high input of energy is required to transform one gram of liquid water into water vapor, an energy requirement called the **heat of vaporization.** Water has a heat of vaporization value of **40.65 kJ/mol**. A

considerable amount of heat energy (586 calories) is required to accomplish this change in water. This process occurs on the surface of water. As liquid water heats up, hydrogen bonding makes it difficult to separate the water molecules from each other, which is required for it to enter its gaseous phase (steam). As a result, water acts as a heat sink, or heat reservoir, and requires much more heat to boil than does a liquid such as ethanol (grain alcohol), whose hydrogen bonding with other ethanol molecules is weaker than water's hydrogen bonding.

The fact that hydrogen bonds need to be broken for water to evaporate means that a substantial amount of energy is used in the process. As the water evaporates, energy is taken up by the process, cooling the environment where the evaporation is taking place. In many living organisms, including humans, the evaporation of sweat, which is 90 percent water, allows the organism to cool so that homeostasis of body temperature can be maintained.

Summary

- The polarity of water and its ability to hydrogen bond contributes to its unique properties.
- Ionic solute molecules are hydrated (surrounded by solvent molecules in a specific orientation).
- Ice is less dense than liquid water due to spaces in the intermolecular structure of ice not present in water.
- Heat capacity is the amount of heat required to raise the temperature of an object by **1°C**).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by **1°C**.
- The dissociation of liquid water molecules, which changes the substance to a gas, requires a lot of energy.

Contributors and Attributions

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- Boundless: The Chemical Foundation of Life
- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: Introductory Chemistry (Tro)
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16.2: Solutions - Homogeneous Mixtures

Learning Objectives

- Learn terminology involving solutions.
- Explain the significance of the statement "like dissolves like."
- 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**. By major and minor we mean whichever component has the greater or lesser presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. However, here we will confine the discussion to solutions for which the major component and the minor component are obvious.



Figure **16.2.1**: Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid $\mathbf{NaCl}$ in liquid water, while air is a solution of a gaseous solute ($\mathbf{O_2}$) in a gaseous solvent ($\mathbf{N_2}$). In all cases, however, the overall phase of the solution is the same phase as the solvent. Table **16.2.1** lists some common types of solutions, with examples of each.

Table **16.2.1**: Types of Solutions

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

Example 16.2.1: Sugar and Water

A solution is made by dissolving 1.00 g of sucrose ($\mathbf{C_{12}H_{22}O_{11}}$) 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 16.2.1

A solution is made by dissolving 3.33 g of $\mathrm{HCl(g)}$ in 40.0 g of liquid methyl alcohol ($\mathrm{CH_3OH}$). Identify the solvent and solute in the resulting solution.

Answer

solute: $\mathrm{HCl(g)}$

solvent: $\mathrm{CH_3OH}$

Like Dissolves Like

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water—it is this oxygen that the fish take in through their gills. The reason we can enjoy carbonated sodas is also due to a nonpolar compound that dissolves in water. Pepsi-cola and all the other sodas have carbon dioxide gas, $\mathrm{CO_2}$, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

Table **16.2.2**: Summary of Solubilities

Solute (Polarity of Compound)	Solvent (Polarity of Compound)	Dominant Intermolecular Force	Is Solution Formed?
Polar	Polar	Dipole-Dipole Force and/or Hydrogen Bond	yes
Non-polar	Non-polar	Dispersion Force	yes
Polar	Non-polar		no
Non-polar	Polar		no
Ionic	Polar	Ion-Dipole	yes
Ionic	Non-polar		no

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges, a solution does not form. When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in 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.



Figure 16.2.2: Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

Example 16.2.2: Polar and Nonpolar Solvents

Would $\mathrm{I_2}$ be more soluble in $\mathrm{CCl_4}$ or $\mathrm{H_2O}$? Explain your answer.

Solution

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

Exercise 16.2.2

Would $\mathrm{C_3H_7OH}$ be more soluble in $\mathrm{CCl_4}$ or $\mathrm{H_2O}$? Explain your answer.

Answer

$\mathrm{H_2O}$, because both experience hydrogen bonding.

Example 16.2.3

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

a. methanol ($\mathrm{CH_3OH}$)
b. sodium sulfate (\ce{Na2SO4}\))
c. octane ($\mathrm{C_8H_{18}}$)

Solution

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

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

Exercise 16.2.3: Toluene

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

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

Answer

Octane ($\mathrm{C_8H_{18}}$) will dissolve. It is also non-polar.

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.

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16.3: The Dissolution Process

Learning Objectives

- To describe the dissolution process at the molecular level

The Dissolution Process

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

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure **16.3.1**. When the solvent is water, the word **hydration**, rather than solvation, is used.

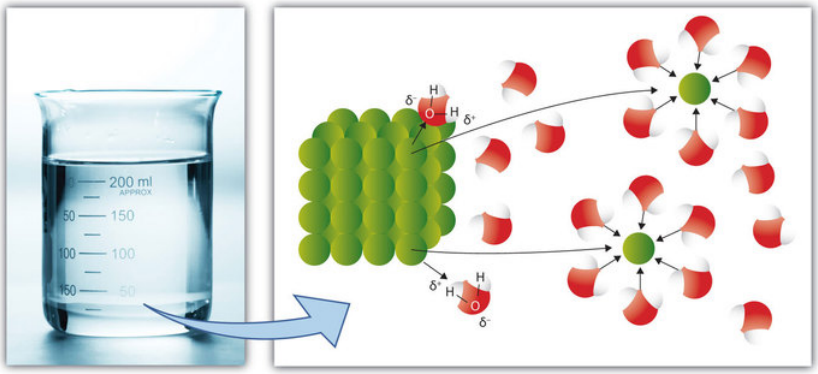


Figure **16.3.1**: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

Ionic Compounds and Covalent Compounds as Solutes

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure **16.3.1**).

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

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

Example 16.3.1

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

1. potassium chloride (KCl)
2. fructose ($C_6H_{12}O_6$)
3. isopropyl alcohol [$CH_3CH(OH)CH_3$]
4. magnesium hydroxide [$Mg(OH)_2$]

Solution

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

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

Exercise 16.3.1

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

a. acetone (CH_3COCH_3)
b. iron(III) nitrate [$Fe(NO_3)_3$]
c. elemental bromine (Br_2)
d. sodium hydroxide (NaOH)

Answer

a. nonelectrolyte

b. electrolyte

c. nonelectrolyte

d. electrolyte

Electrolytes in Body Fluids

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

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

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

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is given when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most

important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

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

Gatorade

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



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

Key Takeaway

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

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16.4: Solutions of Solids Dissolved in Water- How to Make Rock Candy

Learning Objectives

- Define electrolytes and non electrolytes
- Explain why solutions form.
- Discuss the idea of water as the "universal solvent".
- Explain how water molecules attract ionic solids when they dissolve in water.

We have learned that solutions can be formed in a variety of combinations using solids, liquids, and gases. We also know that solutions have constant composition, and that this composition can be varied up to a point to maintain the homogeneous nature of the solution. But how exactly do solutions form? Why is it that oil and water will not form a solution, and yet vinegar and water will? Why could we dissolve table salt in water, but not in vegetable oil? The reasons why solutions will form will be explored in this section, along with a discussion of why water is used most frequently to dissolve substances of various types.

Solubility and Saturation

Table salt (**NaCl**) readily dissolves in water. In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is specified as 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 **16.4.1** 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 **16.4.1**: 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. 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.The figure below illustrates the above process and shows the distinction between unsaturated and saturated.

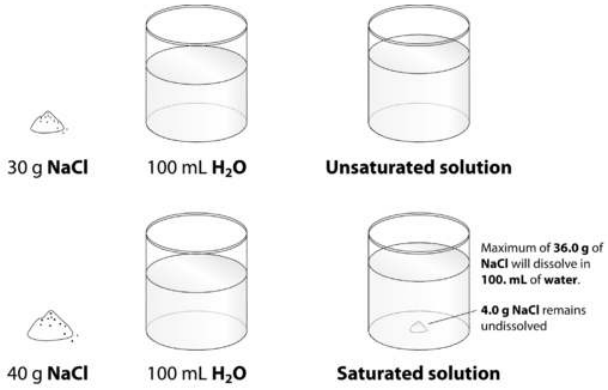


Figure 16.4.1: When 30.0 g of NaCl is added to 100 mL, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution.

How can you tell if a solution is saturated or unsaturated? If more solute is added and it does not dissolve, then the original solution was saturated. If the added solute dissolves, then the original solution was unsaturated. A solution that has been allowed to reach equilibrium, but which has extra undissolved solute at the bottom of the container, must be saturated.



Electrolyte Solutions: Dissolved Ionic Solids

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte (good conductor). If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, the substance is a weak electrolyte (does not conduct electricity as well).

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 16.4.1).

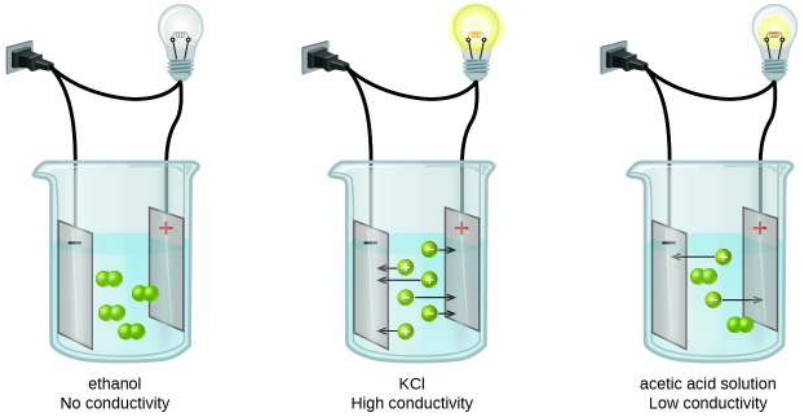


Figure **16.4.1**: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram shows three separate beakers. Each has a wire plugged into a wall outlet. In each case, the wire leads from the wall to the beaker and is split resulting in two ends. One end leads to a light bulb and continues on to a rectangle labeled with a plus sign. The other end leads to a rectangle labeled with a minus sign. The rectangles are in a solution. In the first beaker, labeled “Ethanol No Conductivity,” four pairs of linked small green spheres suspended in the solution between the rectangles. In the second beaker, labeled “K C l Strong Conductivity,” six individual green spheres, three labeled plus and three labeled minus are suspended in the solution. Each of the six spheres has an arrow extending from it pointing to the rectangle labeled with the opposite sign. In the third beaker, labeled “Acetic acid solution Weak conductivity,” two pairs of joined green spheres and two individual spheres, one labeled plus and one labeled minus are shown suspended between the two rectangles. The plus labeled sphere has an arrow pointing to the rectangle labeled minus and the minus labeled sphere has an arrow pointing to the rectangle labeled plus.

Water and other polar molecules are attracted to ions, as shown in Figure **16.4.2**. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

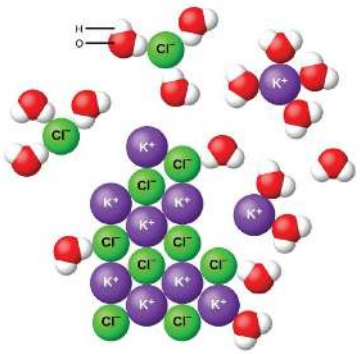


Figure **16.4.2**: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight green spheres labeled C l superscript minus mixed and touching near the center of the diagram. Outside of this cluster of spheres are seventeen clusters of three spheres, which include one red and two white spheres. A red sphere in one of these clusters is labeled O. A white sphere is labeled H. Two of the green C l superscript minus spheres are surrounded by three of the red and white clusters, with the red spheres closer to the green spheres than the white spheres. One of the K superscript plus purple spheres is surrounded by four of the red and white clusters. The white spheres of these clusters are closest to the purple spheres.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Example 16.4.1: Identifying Ionic Compounds

Which compound(s) will dissolve in solution to separate into ions?

a. **LiF**
b. **P_2F_5**
c. **C_2H_5OH**

Solution

LiF will separate into ions when dissolved in solution, because it is an ionic compound. **P_2F_5** and **C_2H_5OH** are both covalent and will stay as molecules in a solution.

Exercise 16.4.1

Which compounds will dissolve in solution to separate into ions?

a. $C_6H_{12}O_{11}$, glucose
b. CCl_4
c. $CaCl_2$
d. $AgNO_3$

Answer

c & d

How Temperature Influences Solubility

The **solubility** of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature. Solubility is often measured as the grams of solute per **100 g** of solvent. The solubility of sodium chloride in water is **36.0 g** per **100 g** water at **20°C**. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubility is specific for a particular solvent. We will consider solubility of material in water as solvent.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (Figure 16.4.4).

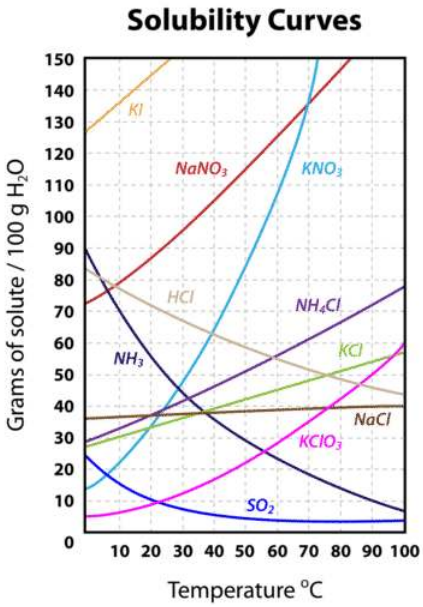


Figure 16.4.4: Solubility curves for several compounds.

Notice how the temperature dependence of $NaCl$ is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of $NaCl$. The curve for KNO_3, on the other hand, is very steep and so an increase in temperature dramatically increases the solubility of KNO_3.

Several substances—HCl, NH_3, and SO_2—have solubility that decreases as temperature increases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increase. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that $80\ g$ of KNO_3 is added to $100\ g$ of water at $30°C$. According to the solubility curve, approximately $48\ g$ of KNO_3 will dissolve at $30°C$. This means that the solution will be saturated since $48\ g$ is less than $80\ g$. We can also determine that there will be $80 - 48 = 32\ g$ of undissolved KNO_3 remaining at the bottom of the container. Now suppose that this saturated solution is heated to $60°C$. According to the curve, the solubility of KNO_3 at $60°C$ is about $107\ g$. Now the solution is unsaturated since it contains only the original $80\ g$ of dissolved solute. Now suppose the solution is cooled all the way down to $0°C$. The solubility at $0°C$ is about $14\ g$, meaning that $80 - 14 = 66\ g$ of the KNO_3 will re-crystallize.

Summary

- Solubility is the specific amount of solute that can dissolve in a given amount of solvent.
- Saturated and unsaturated solutions are defined.
- Ionic compounds dissolve in polar solvents, especially water. This occurs when the positive cation from the ionic solid is attracted to the negative end of the water molecule (oxygen) and the negative anion of the ionic solid is attracted to the positive end of the water molecule (hydrogen).
- Water is considered the universal solvent since it can dissolve both ionic and polar solutes, as well as some nonpolar solutes (in very limited amounts).
- The solubility of a solid in water increases with an increase in temperature.

Vocabulary

- **Miscible** - Liquids that have the ability to dissolve in each other.
- **Immiscible** - Liquids that do not have the ability to dissolve in each other.
- **Electrostatic attraction** - The attraction of oppositely charged particles.

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16.5: Solutions of Gases in Water

Learning Objectives

- Explain how temperature and pressure affect the solubility of gases.

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure **16.5.1**). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

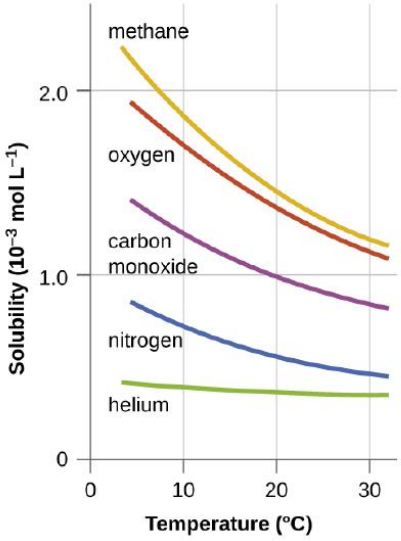


Figure **16.5.1**: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure **16.5.2**).



(a) (b)

Figure 16.5.2: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (Credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service.)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 16.5.3). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

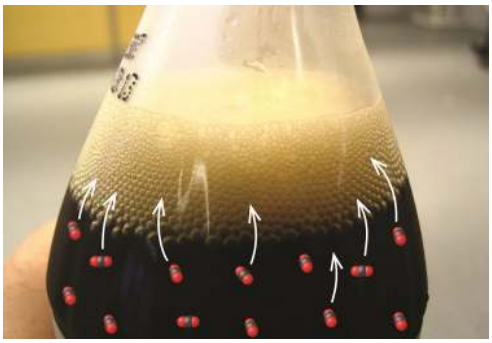


Figure 16.5.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. A dark brown liquid is shown in a clear, colorless container. A thick layer of beige bubbles appear at the surface of the liquid. In the liquid, thirteen small clusters of single black spheres with two red spheres attached to the left and right are shown. Red spheres represent oxygen atoms and black represent carbon atoms. Seven white arrows point upward in the container from these clusters to the bubble layer at the top of the liquid. (Credit: modification of work by Derrick Coetzee.)

"Fizz"

The dissolution in a liquid, also known as fizz, usually involves carbon dioxide under high pressure. When the pressure is reduced, the carbon dioxide is released from the solution as small bubbles, which causes the solution to become effervescent, or fizzy. A common example is the dissolving of carbon dioxide in water, resulting in carbonated water.

Carbon dioxide is weakly soluble in water, therefore it separates into a gas when the pressure is released. This process is generally represented by the following reaction, where a pressurized dilute solution of carbonic acid in water releases gaseous carbon dioxide at decompression:

$$\mathrm{H_2CO_3\,(aq) \longrightarrow H_2O\,(l) + CO_2\,(g)}$$

In simple terms, it is the result of the chemical reaction occurring in the liquid which produces a gaseous product.

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Example 16.5.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g$$

$$\begin{gathered} 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ (\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ = 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{gathered}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 16.5.1

A 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer

7.25×10^{-3} g

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

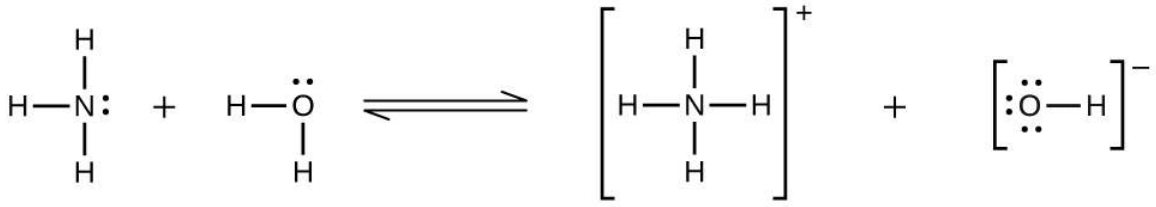
As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow

speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventative measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure **16.5.4**).



Figure **16.5.4**: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy. Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



This reaction diagram shows three H atoms bonded to an N atom above, below, and two the left of the N. A single pair of dots is present on the right side of the N. This is followed by a plus, then two H atoms bonded to an O atom to the left and below the O. Two pairs of dots are present on the O, one above and the other to the right of the O. A double arrow, with a top arrow pointing right and a bottom arrow pointing left follows. To the right of the double arrow, four H atoms are shown bonded to a central N atom. These 5 atoms are enclosed in brackets with a superscript plus outside. A plus follows, then an O atom linked by a bond to an H atom on its right. The O atom has pairs of dots above, to the left, and below the atom. The linked O and H are enclosed in brackets with superscript minus outside.

Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated.

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16.6: Solution Concentration- Mass Percent

Learning Objectives

- Express the amount of solute in a solution in various concentration units.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms with meanings that depend on various factors.

Introduction

Concentration is the measure of how much of a given substance is mixed with another substance. Solutions are said to be either dilute or concentrated. When we say that vinegar is 5% acetic acid in water, we are giving the concentration. If we said the mixture was 10% acetic acid, this would be more concentrated than the vinegar solution.

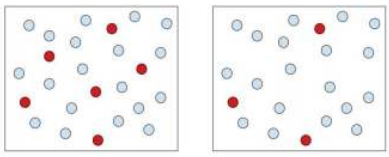


Figure **16.6.1**: The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 Tracy Poulsen).

A **concentrated** solution is one in which there is a large amount of solute in a given amount of solvent. A **dilute** solution is one in which there is a small amount of solute in a given amount of solvent. A dilute solution is a concentrated solution that has been, in essence, watered down. Think of the frozen juice containers you buy in the grocery store. To make juice, you have to mix the frozen juice concentrate from inside these containers with three or four times the container size full of water. Therefore, you are diluting the concentrated juice. In terms of solute and solvent, the concentrated solution has a lot of solute versus the dilute solution that would have a smaller amount of solute.

The terms "concentrated" and "dilute" provide qualitative methods of describing concentration. Although qualitative observations are necessary and have their place in every part of science, including chemistry, we have seen throughout our study of science that there is a definite need for quantitative measurements in science. This is particularly true in solution chemistry. In this section, we will explore some quantitative methods of expressing solution concentration.

Mass Percent

There are several ways of expressing the concentration of a solution by using a percentage. The mass/mass percent (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\,\text{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

mass of solution = mass of solute + mass solvent

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Suppose that a solution was prepared by dissolving $25.0\ \text{g}$ of sugar into $100.0\ \text{g}$ of water.

The mass of the solution is

mass of solution = 25.0g sugar + 100.0g water = 125.0 g

The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25.0\ \text{g sugar}}{125.0\ \text{g solution}} \times 100\% = 20.0\%\ \text{sugar}$$

Example 16.6.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

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

Exercise 16.6.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90 %

Using Mass Percent in Calculations

Sometimes you may want to make up a particular mass of solution of a given percent by mass and need to calculate what mass of the solute to use. Using mass percent as a conversion can be useful in this type of problem. The mass percent can be expressed as a conversion factor in the form $\frac{g\ \text{solute}}{100\ \text{gsolution}}$ or $\frac{100\ \text{gsolution}}{g\ \text{solute}}$

For example, if you need to make $3000.0\ \mathrm{g}$ of a 5.00% solution of sodium chloride, the mass of solute needs to be determined.

Solution

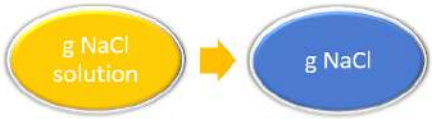
Given: 3000.0 g NaCl solution

5.00% NaCl solution

Find: mass of solute = ? g NaCl

Other known quantities: 5.00 g NaCl is to 100 g solution

The appropriate conversion factor (based on the given mass percent) can be used follows:



$$\frac{5.00\ g\ NaCl}{100\ g\ NaCl\ solution}$$

To solve for the mass of NaCl, the given mass of solution is multiplied by the conversion factor.

$$gNaCl = 3,000.0\ \cancel{g\ NaCl\ solution} \times \frac{5.00\ g\ NaCl}{100\ \cancel{g\ NaCl\ solution}} = 150.0 g\ NaCl$$

You would need to weigh out $150\ \mathrm{g}$ of NaCl and add it to $2850\ \mathrm{g}$ of water. Notice that it was necessary to subtract the mass of the NaCl $(150\ \mathrm{g})$ from the mass of solution $(3000\ \mathrm{g})$ to calculate the mass of the water that would need to be added.

Exercise 16.6.1

What is the amount (in g) of hydrogen peroxide (H_2O_2) needed to make a 6.00 kg, 3.00 % (by mass) H_2O_2 solution?

Answer

180 g H_2O_2

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16.7: Solution Concentration- Molarity

Learning Objectives

- Use molarity to determine quantities in chemical reactions.
- Use molarity as a conversion factor in calculations.

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Of all the quantitative measures of concentration, molarity is the one used most frequently by chemists. **Molarity** is defined as the number of moles of solute per liter of solution.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{16.7.1}$$

The symbol for molarity is **M** or moles/liter. Chemists also use square brackets to indicate a reference to the molarity of a substance. For example, the expression $[Ag^+]$ refers to the molarity of the silver ion in solution. Solution concentrations expressed in molarity are the easiest to perform calculations with, but the most difficult to make in the lab. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl (aq).” This is read as "a 3.00 ***molar*** sodium chloride solution," meaning that there are 3.00 moles of NaOH dissolved per one liter of solution.

> *Be sure to note that molarity is calculated as the total volume of the **entire** solution, not just volume of solvent! The solute contributes to total volume.*

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?

Step 1: First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4 \, \cancel{g HCl} \times \frac{1 \, mol \, HCl}{36.5 \, \cancel{g HCl}} = 0.614 \, mol \, HCl$$

Step 2: Now we can use the definition of molarity to determine a concentration:

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

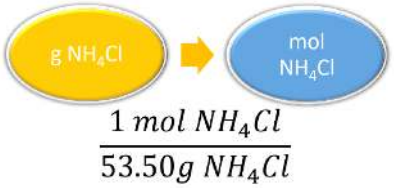
Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

Example 16.7.1

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

Solution

Solutions to Example 13.6.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Mass $= 42.23\ \text{g}\ NH_4Cl$ Volume solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$ Find: Molarity = ? M
List other known quantities.	Molar mass $NH_4Cl = 53.50\ \text{g/mol}$
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles.  $\frac{1\ mol\ NH_4Cl}{53.50g\ NH_4Cl}$ 2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters. $\text{M} = \frac{\text{mol } NH_4Cl}{\text{L solution}}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $42.23\ \cancel{\text{g } NH_4Cl} \times \frac{1\ \text{mol } NH_4Cl}{53.50\ \cancel{\text{g } NH_4Cl}} = 0.7893\ \text{mol } NH_4Cl$ $\frac{0.7893\ \text{mol } NH_4Cl}{0.5000\ \text{L solution}} = 1.579\ \text{M}$
Think about your result.	The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain $1.579\ \text{mol } NH_4Cl$. Four significant figures are appropriate.

? Exercise 16.7.1A

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M $C_6H_{12}O_6$

? Exercise 16.7.1B

What is the concentration, in mol/L, where $137\ \text{g}$ of $NaCl$ has been dissolved in enough water to make $500\ \text{mL}$ of solution?

Answer

4.69 M NaCl

Using Molarity in Calculations

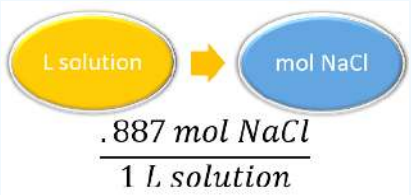
Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition.

Example 16.7.2: Determining Moles of Solute, Given the Concentration and Volume of a Solution

For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

Solution



$$0.108 \cancel{L\ solution} \times \frac{0.887\ mol\ NaCl}{1 \cancel{L\ solution}} = 0.0958\ mol\ NaCl$$

If we used the definition approach, we get the same answer, but now we are using conversion factor skills.

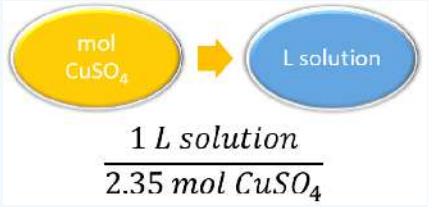
Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 16.7.3: Determining Volume of a Solution, Given the Concentration and Moles of Solute

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:



$$4.88 \cancel{mol\ CuSO_4} \times \frac{1\ L\ solution}{2.35 \cancel{mol\ CuSO_4}} = 2.08\ L\ of\ solution$$

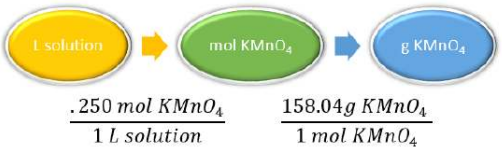
In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams. The following example illustrates this.

Example 16.7.4

A chemist needs to prepare **3.00 L** of a **0.250 M** solution of potassium permanganate (**$KMnO_4$**). What mass of **$KMnO_4$** does she need to make the solution?

Solution

Solutions to Example 13.6.4

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Molarity $= 0.250\ \mathrm{M}$ Volume $= 3.00\ \mathrm{L}$ Find: Mass $\mathrm{KMnO_4} = ?\ \mathrm{g}$
List other known quantities.	Molar mass $\mathrm{KMnO_4} = 158.04\ \mathrm{g/mol}$ 0.250 mol $KMnO_4$ to 1 L of $KMnO_4$ solution
Plan the problem.	 $\frac{.250\ mol\ KMnO_4}{1\ L\ solution}$ $\frac{158.04g\ KMnO_4}{1\ mol\ KMnO_4}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $\mathrm{mol\ KMnO_4} = 0.250\ \mathrm{M\ KMnO_4} \times 3.00\ \mathrm{L} = 0.750\ \mathrm{mol\ KMnO_4}$ $3.00\ \cancel{L\ solution} \times \frac{0.250\ \cancel{\mathrm{mol\ KMnO_4}}}{1\ \cancel{L\ solution}} \times \frac{158.04\ \mathrm{g\ KMnO_4}}{1\ \cancel{\mathrm{mol\ KMnO_4}}} = 119\ \mathrm{g\ KMnO_4}$
Think about your result.	When $119\ \mathrm{g}$ of potassium permanganate is dissolved into water to make $3.00\ \mathrm{L}$ of solution, the molarity is $0.250\ \mathrm{M}$.

Exercise 16.7.4*A*

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer

1.74 L

Exercise 16.7.4*B*

Answer the problems below using concentration as a conversion factor.

a. What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?
b. What volume of 1.50 M HCl solution contains 10.0 g of hydrogen chloride?

Answer a

6.12 g

Answer b

183 mL or 0.183L

How to Indicate Concentration

- Square brackets are often used to represent concentration, e.g., [NaOH] = 0.50 M.
- Use the capital letter M for molarity, not a lower case m (this is a different concentration unit called *molality*).



Watch as the Flinn Scientific Tech Staff demonstrates "How To Prepare Solutions."

It is important to note that there are many different ways you can set up and solve your chemistry equations. Some students prefer to answer multi-step calculations in one long step, while others prefer to work out each step individually. Neither method is necessarily better or worse than the other method—whichever makes the most sense to ***you*** is the one that you should use. In this text, we will typically use unit analysis (also called dimension analysis or factor analysis).

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16.8: Solution Dilution

Learning Objectives

- Explain how concentrations can be changed in the lab.
- Understand how stock solutions are used in the laboratory.

We are often concerned with how much solute is dissolved in a given amount of solution. We will begin our discussion of solution concentration with two related and relative terms: **dilute** and **concentrated**.

- A **dilute** solution is one in which there is a relatively small amount of solute dissolved in the solution.
- A **concentrated** solution contains a relatively large amount of solute.

These two terms do not provide any quantitative information (actual numbers), but they are often useful in comparing solutions in a more general sense. These terms also do not tell us whether or not the solution is saturated or unsaturated, or whether the solution is "strong" or "weak". These last two terms will have special meanings when we discuss acids and bases, so be careful not to confuse them.

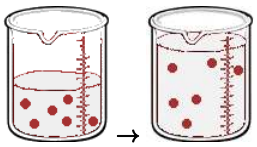
Stock Solutions

It is often necessary to have a solution with a concentration that is very precisely known. Solutions containing a precise mass of solute in a precise volume of solution are called **stock (or standard) solutions.** To prepare a standard solution, a piece of lab equipment called a volumetric flask should be used. These flasks range in size from 10 mL to 2000 mL and are carefully calibrated to a single volume. On the narrow stem is a **calibration mark**. The precise mass of solute is dissolved in a bit of the solvent, and this is added to the flask. Then, enough solvent is added to the flask until the level reaches the calibration mark.

Often, it is convenient to prepare a series of solutions of known concentrations by first preparing a single **stock solution**, as described in the previous section. **Aliquots** (carefully measured volumes) of the stock solution can then be diluted to any desired volume. In other cases, it may be inconvenient to weigh a small mass of sample accurately enough to prepare a small volume of a dilute solution. Each of these situations requires that a solution be diluted to obtain the desired concentration.

Dilutions of Stock (or Standard) Solutions

Imagine we have a salt water solution with a certain concentration. That means we have a certain amount of salt (a certain mass or a certain number of moles) dissolved in a certain volume of solution. Next, we will dilute this solution. This is done by adding more water, not more salt:



Before Dilution and After Dilution

The molarity of solution 1 is

$$M_1 = \frac{\text{moles}_1}{\text{liter}_1}$$

and the molarity of solution 2 is

$$M_2 = \frac{\text{moles}_2}{\text{liter}_2}$$

rearrange the equations to find moles:

$$\text{moles}_1 = M_1 \text{liter}_1$$

and

$$\text{moles}_2 = M_2\text{liter}_2$$

What stayed the same and what changed between the two solutions? By adding more water, we changed the volume of the solution. Doing so also changed its concentration. **However, the number of moles of solute did not change.** So,

$$moles_1 = moles_2$$

Therefore

$$\boxed{M_1V_1 = M_2V_2} \tag{16.8.1}$$

where

- M_1 and M_2 are the concentrations of the original and diluted solutions
- V_1 and V_2 are the volumes of the two solutions

Preparing dilutions is a common activity in the chemistry lab and elsewhere. Once you understand the above relationship, the calculations are simple.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

Another common dilution problem involves calculating what amount of a highly concentrated solution is required to make a desired quantity of solution of lesser concentration. The highly concentrated solution is typically referred to as the stock solution.

Example 16.8.1: Diluting Nitric Acid

Nitric acid (HNO_3) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is $16\ \text{M}$. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

Solution

Solutions to Example13.7.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: M_1, Stock $\text{HNO}_3 = 16\ \text{M}$ $V_2 = 8.00\ \text{L}$ $M_2 = 0.50\ \text{M}$ Find: Volume stock HNO_3 $(V_1) = ?\ \text{L}$
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_1. $$V_1 = \frac{M_2 \times V_2}{M_1}$$
Calculate and cancel units.	Now substitute the known quantities into the equation and solve. $$V_1 = \frac{0.50\ \text{M} \times 8.00\ \text{L}}{16\ \text{M}} = 0.25\ \text{L} \tag{16.8.2}$$
Think about your result.	$0.25\ \text{L}$ $(250\ \text{mL})$ of the stock HNO_3 needs to be diluted with water to a final volume of $8.00\ \text{L}$. The dilution is by a factor of 32 to go from $16\ \text{M}$ to $0.5\ \text{M}$.

Exercise 16.8.1

A 0.885 M solution of KBr with an initial volume of 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

135.4 mL

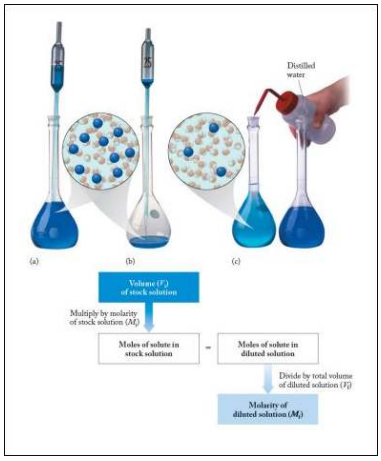
Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).

Diluting and Mixing Solutions

Diluting and Mixing Solutions



How to Dilute a Solution by CarolinaBiological



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16.9: Freezing Point Depression and Boiling Point Elevation

Learning Objectives

- Explain what the term "colligative" means, and list the colligative properties.
- Indicate what happens to the boiling point and the freezing point of a solvent when a solute is added to it.
- Calculate boiling point elevations and freezing point depressions for a solution.

People who live in colder climates have seen trucks put salt on the roads when snow or ice is forecast. Why is this done? As a result of the information you explore in this section, you will understand why these events occur. You will also learn to calculate exactly how much of an effect a specific solute can have on the boiling point or freezing point of a solution.

The example given in the introduction is an example of a colligative property. **Colligative properties** are properties that differ based on the concentration of solute in a solvent, but not on the type of solute. What this means for the example above is that people in colder climates do not necessarily need salt to get the same effect on the roads—any solute will work. However, the higher the concentration of solute, the more these properties will change.

Boiling Point Elevation

Water boils at $100°C$ at $1\ atm$ of pressure, but a solution of saltwater does not . When table salt is added to water, the resulting solution has a higher boiling point than the water did by itself. The ions form an attraction with the solvent particles that prevents the water molecules from going into the gas phase. Therefore, the saltwater solution will not boil at $100°C$. In order for the saltwater solution to boil, the temperature must be raised about $100°C$. This is true for any solute added to a solvent; the boiling point will be higher than the boiling point of the pure solvent (without the solute). In other words, when anything is dissolved in water, the solution will boil at a higher temperature than pure water would.

The boiling point elevation due to the presence of a solute is also a colligative property. That is, the amount of change in the boiling point is related to the number of particles of solute in a solution and is not related to the chemical composition of the solute. A $0.20\ m$ solution of table salt and a $0.20\ m$ solution of hydrochloric acid would have the same effect on the boiling point.

Freezing Point Depression

The effect of adding a solute to a solvent has the opposite effect on the freezing point of a solution as it does on the boiling point. A solution will have a lower freezing point than a pure solvent. The **freezing point** is the temperature at which the liquid changes to a solid. At a given temperature, if a substance is added to a solvent (such as water), the solute-solvent interactions prevent the solvent from going into the solid phase. The solute-solvent interactions require the temperature to decrease further in order to solidify the solution. A common example is found when salt is used on icy roadways. Salt is put on roads so that the water on the roads will not freeze at the normal $0°C$ but at a lower temperature, as low as $-9°C$. The de-icing of planes is another common example of freezing point depression in action. A number of solutions are used, but commonly a solution such as ethylene glycol, or a less toxic monopropylene glycol, is used to de-ice an aircraft. The aircrafts are sprayed with the solution when the temperature is predicted to drop below the freezing point. The **freezing point depression** is the difference in the freezing points of the solution from the pure solvent. This is true for any solute added to a solvent; the freezing point of the solution will be lower than the freezing point of the pure solvent (without the solute). Thus, when anything is dissolved in water, the solution will freeze at a lower temperature than pure water would.

The freezing point depression due to the presence of a solute is also a colligative property. That is, the amount of change in the freezing point is related to the number of particles of solute in a solution and is not related to the chemical composition of the solute. A $0.20\ m$ solution of table salt and a $0.20\ m$ solution of hydrochloric acid would have the same effect on the freezing point.

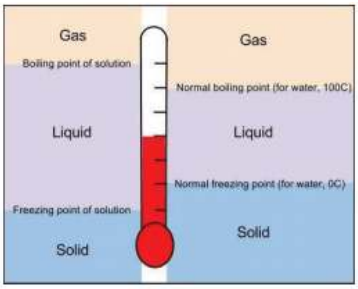


Figure **16.9.1**: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Comparing the Freezing and Boiling Point of Solutions

Recall that covalent and ionic compounds do not dissolve in the same way. Ionic compounds break up into cations and anions when they dissolve. Covalent compounds typically do not break up. For example a sugar/water solution stays as sugar and water, with the sugar molecules staying as molecules. Remember that colligative properties are due to the number of solute particles in the solution. Adding 10 molecules of sugar to a solvent will produce 10 solute particles in the solution. When the solute is ionic, such as $\mathbf{NaCl}$ however, adding 10 formulas of solute to the solution will produce 20 ions (solute particles) in the solution. Therefore, adding enough $\mathbf{NaCl}$ solute to a solvent to produce a $\mathbf{0.20\ m}$ solution will have twice the effect of adding enough sugar to a solvent to produce a $\mathbf{0.20\ m}$ solution. Colligative properties depend on the number of solute particles in the solution.

"i" is the number of particles that the solute will dissociate into upon mixing with the solvent. For example, sodium chloride, $\mathbf{NaCl}$, will dissociate into two ions so for $\mathbf{NaCl}$, $i = 2$; for lithium nitrate, $\mathbf{LiNO_3}$, $i = 2$; and for calcium chloride, $\mathbf{CaCl_2}$, $i = 3$. For covalent compounds, i is always equal to 1.

By knowing the *molality* of a solution and the number of particles a compound will dissolve to form, it is possible to predict which solution in a group will have the lowest freezing point. To compare the boiling or freezing points of solutions, follow these general steps:

1. Label each solute as ionic or covalent.
2. If the solute is ionic, determine the number of *ions* in the formula. Be careful to look for polyatomic ions.
3. Multiply the original molality ($\mathbf{m}$) of the solution by the number of particles formed when the solution dissolves. This will give you the total concentration of particles dissolved.
4. Compare these values. The higher total concentration will result in a higher boiling point and a lower freezing point.

✔ Example 16.9.1

Rank the following solutions in water in order of *increasing* (lowest to highest) freezing point:

- $\mathbf{0.1\ m\ NaCl}$
- $\mathbf{0.1\ m\ C_6H_{12}O_6}$
- $\mathbf{0.1\ m\ CaI_2}$

Solution

To compare freezing points, we need to know the total concentration of all particles when the solute has been dissolved.

- $\mathbf{0.1\ m\ NaCl}$: This compound is ionic (metal with nonmetal), and will dissolve into 2 parts. The total final concentration is: $\mathbf{(0.1\ m)\,(2) = 0.2\ m}$
- $\mathbf{0.1\ m\ C_6H_{12}O_6}$: This compound is covalent (nonmetal with nonmetal), and will stay as 1 part. The total final concentration is: $\mathbf{(0.1\ m)\,(1) = 0.1\ m}$
- $\mathbf{0.1\ m\ CaI_2}$: This compound is ionic (metal with nonmetal), and will dissolve into 3 parts. The total final concentration is: $\mathbf{(0.1\ m)\,(3) = 0.3\ m}$

Remember, the greater the concentration of particles, the lower the freezing point will be. $\mathbf{0.1\ m\ CaI_2}$ will have the lowest freezing point, followed by $\mathbf{0.1\ m\ NaCl}$, and the highest of the three solutions will be $\mathbf{0.1\ m\ C_6H_{12}O_6}$, but all three of them will have a lower freezing point than pure water.

The boiling point of a solution is higher than the boiling point of a pure solvent, and the freezing point of a solution is lower than the freezing point of a pure solvent. However, the amount to which the boiling point increases or the freezing point decreases depends on the amount of solute that is added to the solvent. A mathematical equation is used to calculate the boiling point elevation or the freezing point depression.

The boiling point elevation is the amount that the boiling point temperature *increases* compared to the original solvent. For example, the boiling point of pure water at $1.0\ \text{atm}$ is $100°\text{C}$ while the boiling point of a 2% saltwater solution is about $102°\text{C}$. Therefore, the boiling point elevation would be $2°\text{C}$. The freezing point depression is the amount that the freezing temperature *decreases*.

Both the boiling point elevation and the freezing point depression are related to the molality of the solution. Looking at the formula for the boiling point elevation and freezing point depression, we see similarities between the two. The equation used to calculate the increase in the boiling point is:

$$\Delta T_b = k_b \cdot \text{m} \cdot i \tag{16.9.1}$$

Where:

- $\Delta T_b =$ the amount the boiling point increases.
- $k_b =$ the boiling point elevation constant which depends on the solvent (for water, this number is $0.515°\text{C/m}$).
- $\text{m} =$ the molality of the solution.
- $i =$ the number of particles formed when that compound dissolves (for covalent compounds, this number is always 1).

The following equation is used to calculate the decrease in the freezing point:

$$\Delta T_f = k_f \cdot \text{m} \cdot i \tag{16.9.2}$$

Where:

- $\Delta T_f =$ the amount the freezing temperature decreases.
- $k_f =$ the freezing point depression constant which depends on the solvent (for water, this number is $1.86°\text{C/m}$).
- $\text{m} =$ the molality of the solution.
- $i =$ the number of particles formed when that compound dissolves (for covalent compounds, this number is always 1).

Example 16.9.2: Adding Antifreeze to Protein Engines

Antifreeze is used in automobile radiators to keep the coolant from freezing. In geographical areas where winter temperatures go below the freezing point of water, using pure water as the coolant could allow the water to freeze. Since water expands when it freezes, freezing coolant could crack engine blocks, radiators, and coolant lines. The main component in antifreeze is ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$. What is the concentration of ethylene glycol in a solution of water, in molality, if the freezing point dropped by $2.64°\text{C}$? The freezing point constant, k_f, for water is $1.86°\text{C/m}$.

Solution

Use the equation for freezing point depression of solution (Equation 16.9.2):

$$\Delta T_f = k_f \cdot \text{m} \cdot i$$

Substituting in the appropriate values we get:

$$2.64°\text{C} = (1.86°\text{C/m})\,(\text{m})\,(1)$$

Solve for m by dividing both sides by $1.86°\text{C/m}$.

$$\text{m} = 1.42$$

Example 16.9.3: Adding Salt to Elevate Boiling Temperature

A solution of $10.0\ \text{g}$ of sodium chloride is added to $100.0\ \text{g}$ of water in an attempt to elevate the boiling point. What is the boiling point of the solution? k_b for water is 0.52°C/m.

Solution

Use the equation for boiling point elevation of solution (Equation 16.9.1):

$$\Delta T_b = k_b \cdot \text{m} \cdot i$$

We need to be able to substitute each variable into this equation.

- $k_b = 0.52^\circ\text{C/m}$
- m: We must solve for this using stoichiometry. Given: $10.0\ \text{g NaCl}$ and $100.0\ \text{g H}_2\text{O}$ Find: $\text{mol NaCl/kg H}_2\text{O}$. Ratios: molar mass of NaCl, $1000\ \text{g} = 1\ \text{kg}$

$$\frac{10.0\ \cancel{\text{g NaCl}}}{100.0\ \cancel{\text{g H}_2\text{O}}} \cdot \frac{1\ \text{mol NaCl}}{58.45\ \cancel{\text{g NaCl}}} \cdot \frac{1000\ \cancel{\text{g H}_2\text{O}}}{1\ \text{kg H}_2\text{O}} = 1.71\ \text{m}$$

- For NaCl, $i = 2$

Substitute these values into the equation $\Delta T_b = k_b \cdot \text{m} \cdot i$. We get:

$$\Delta T_b = \left(0.52 \frac{^\circ\text{C}}{\cancel{\text{m}}}\right)(1.71\ \cancel{\text{m}})\,(2) = 1.78^\circ\text{C}$$

Water normally boils at 100°C, but our calculation shows that the boiling point increased by 1.78°C. Our new boiling point is 101.78°C.

Note: Since sea water contains roughly 28.0 g of NaCl per liter, this saltwater solution is approximately **four times** more concentrated than sea water (all for a 2° C rise of boiling temperature).

Summary

- Colligative properties are properties that are due only to the number of particles in solution, and are not related to the chemical properties of the solute.
- Boiling points of solutions are higher than the boiling points of the pure solvents.
- Freezing points of solutions are lower than the freezing points of the pure solvents.
- Ionic compounds split into ions when they dissolve, forming more particles. Covalent compounds stay as complete molecules when they dissolve.

Vocabulary

- **Colligative property** - A property that is due only to the number of particles in solution, and not the type of the solute.
- **Boiling point elevation** - The amount that the boiling point of a solution increases from the boiling point of the pure solvent.
- **Freezing point depression** - The amount that the freezing point of a solution decreases from the freezing point of the pure solvent.

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16.10: Osmosis and Diffusion

Learning Outcomes

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions.
- Describe a semipermeable membrane.
- Predict behavior of blood cells in different solution types.
- Describe flow of solvent molecules across a membrane.
- Identify the polar and nonpolar regions of a cell membrane.
- Explain the components present in a phospholipid.

Fish cells, like all cells, have semipermeable membranes. Eventually, the concentration of "stuff" on either side of them will even out. A fish that lives in salt water will have somewhat salty water inside itself. Put it in freshwater, and the freshwater will, through osmosis, enter the fish, causing its cells to swell, and the fish will die. What will happen to a freshwater fish in the ocean?

Osmosis

Imagine you have a cup that has $100\ \text{mL}$ water, and you add $15\ \text{g}$ of table sugar to the water. The sugar dissolves and the mixture that is now in the cup is made up of a **solute** (the sugar) that is dissolved in the **solvent** (the water). The mixture of a solute in a solvent is called a **solution**.

Imagine now that you have a second cup with $100\ \text{mL}$ of water, and you add $45\ \text{g}$ of table sugar to the water. Just like the first cup, the sugar is the solute, and the water is the solvent. But now you have two mixtures of different solute concentrations. In comparing two solutions of unequal solute concentration, the solution with the higher solute concentration is **hypertonic**, and the solution with the lower solute concentration is **hypotonic**. Solutions of equal solute concentration are **isotonic**. The first sugar solution is hypotonic to the second solution. The second sugar solution is hypertonic to the first.

You now add the two solutions to a beaker that has been divided by a semipermeable membrane, with pores that are too small for the sugar molecules to pass through, but are big enough for the water molecules to pass through. The hypertonic solution is one side of the membrane and the hypotonic solution on the other. The hypertonic solution has a lower water concentration than the hypotonic solution, so a concentration gradient of water now exists across the membrane. Water molecules will move from the side of higher water concentration to the side of lower concentration until both solutions are isotonic. At this point, **equilibrium** is reached.

Red blood cells behave the same way (see figure below). When red blood cells are in a hypertonic (higher concentration) solution, water flows out of the cell faster than it comes in. This results in *crenation* (shriveling) of the blood cell. On the other extreme, a red blood cell that is hypotonic (lower concentration outside the cell) will result in more water flowing into the cell than out. This results in swelling of the cell and potential *hemolysis* (bursting) of the cell. In an isotonic solution, the flow of water in and out of the cell is happening at the same rate.

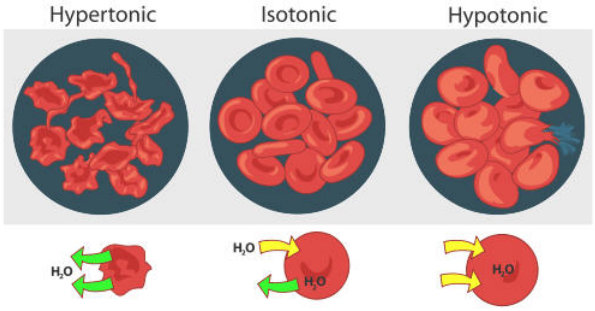


Figure 9.7.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

Osmosis is the diffusion of water molecules across a semipermeable membrane from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water). Water moves into and

out of cells by osmosis.

- If a cell is in a hypertonic solution, the solution has a lower water concentration than the cell cytosol, and water moves out of the cell until both solutions are isotonic.
- Cells placed in a hypotonic solution will take in water across their membranes until both the external solution and the cytosol are isotonic.

A red blood cell will swell and undergo hemolysis (burst) when placed in a hypotonic solution. When placed in a hypertonic solution, a red blood cell will lose water and undergo *crenation* (shrivel). Animal cells tend to do best in an isotonic environment, where the flow of water in and out of the cell is occurring at equal rates.

Diffusion

Passive transport is a way that small molecules or ions move across the cell membrane without input of energy by the cell. The three main kinds of passive transport are diffusion (or simple diffusion), osmosis, and facilitated diffusion. Simple diffusion and osmosis do not involve transport proteins. Facilitated diffusion requires the assistance of proteins.

Diffusion is the movement of molecules from an area of high concentration of the molecules to an area with a lower concentration. For cell transport, diffusion is the movement of small molecules across the cell membrane. The difference in the concentrations of the molecules in the two areas is called the **concentration gradient**. The kinetic energy of the molecules results in random motion, causing diffusion. In simple diffusion, this process proceeds without the aid of a transport protein. It is the random motion of the molecules that causes them to move from an area of high concentration to an area with a lower concentration.

Diffusion will continue until the concentration gradient has been eliminated. Since diffusion moves materials from an area of higher concentration to the lower, it is described as moving solutes "down the concentration gradient". The end result is an equal concentration, or **equilibrium**, of molecules on both sides of the membrane. At equilibrium, movement of molecules does not stop. At equilibrium, there is equal movement of materials in both directions.

Not everything can make it into your cells. Your cells have a plasma membrane that helps to guard your cells from unwanted intruders.

The Plasma Membrane and Cytosol

If the outside environment of a cell is water-based, and the inside of the cell is also mostly water, something has to make sure the cell stays intact in this environment. What would happen if a cell dissolved in water, like sugar does? Obviously, the cell could not survive in such an environment. So something must protect the cell and allow it to survive in its water-based environment. All cells have a barrier around them that separates them from the environment and from other cells. This barrier is called the **plasma membrane**, or cell membrane.

The Plasma Membrane

The plasma membrane (see figure below) is made of a double layer of special lipids, known as **phospholipids**. The phospholipid is a lipid molecule with a hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails. Because of the hydrophilic and hydrophobic nature of the phospholipid, the molecule must be arranged in a specific pattern as only certain parts of the molecule can physically be in contact with water. Remember that there is water outside the cell, and the **cytoplasm** inside the cell is mostly water as well. So the phospholipids are arranged in a double layer (a bilayer) to keep the cell separate from its environment. Lipids do not mix with water (recall that oil is a lipid), so the phospholipid bilayer of the cell membrane acts as a barrier, keeping water out of the cell, and keeping the cytoplasm inside the cell. The cell membrane allows the cell to stay structurally intact in its water-based environment.

The function of the plasma membrane is to control what goes in and out of the cell. Some molecules can go through the cell membrane to enter and leave the cell, but some cannot. The cell is therefore not completely permeable. "Permeable" means that anything can cross a barrier. An open door is completely permeable to anything that wants to enter or exit through the door. The plasma membrane is **semipermeable**, meaning that some things can enter the cell, and some things cannot.

Molecules that cannot easily pass through the bilayer include ions and small hydrophilic molecules, such as glucose, and macromolecules, including proteins and RNA. Examples of molecules that can easily diffuse across the plasma membrane include

carbon dioxide and oxygen gas. These molecules diffuse freely in and out of the cell, along their concentration gradient. Though water is a polar molecule, it can also diffuse through the plasma membrane.

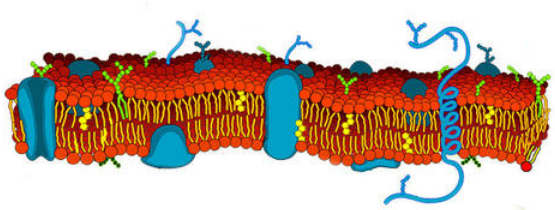


Figure 9.7.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side of the bilayer. There are many proteins throughout the membrane.

Cytosol

The inside of all cells also contain a jelly-like substance called **cytosol**. Cytosol is composed of water and other molecules, including **enzymes**, which are proteins that speed up the cell's chemical reactions. Everything in the cell sits in the cytosol, like fruit in a Jell-o mold. The term cytoplasm refers to the cytosol and all of the organelles, the specialized compartments of the cell. The cytoplasm does not include the nucleus. As a prokaryotic cell does not have a nucleus, the DNA is in the cytoplasm.

Supplemental Resources

- The Plasma Membrane: www.youtube.com/watch?v=moPJkCbKjBs

Key Takeaways

- Water moves into and out of cells by osmosis.
- Water (solvent) moves from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water).

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CHAPTER OVERVIEW

17: Acids and Bases

17.1: Acids and Bases - Experimental Definitions
17.2: Acids, Bases, and Salts
17.3: Acidic and Basic Anhydrides
17.4: Strong and Weak Acids and Bases
17.5: Neutralization
17.6: The pH Scale
17.7: Buffers and Conjugate Acid-Base Pairs
17.8: Acids and Bases in Industry and in Daily Life
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17.10: All-Purpose and Special Purpose Cleaning Products

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17.1: Acids and Bases - Experimental Definitions

Learning Objectives

- Examine properties of acids and bases.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee.

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the **HCl** in the stomach and neutralize it, taking care of that unpleasant feeling. Figure **17.1.1** provides some examples of acids and bases.



Figure **17.1.1** Some examples of common household acids and bases.

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicators. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{17.1.1}$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.

Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.



Figure 17.1.2 Phenolphthalein indicator in presence of base.

Warning

Tasting chemicals and touching them are NOT good lab practices and should be avoided - in other words, don't do this at home.

Summary

- A brief summary of properties of acids and bases are given.
- Properties of acids and bases mostly contrast each other.

Contributors and Attributions

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

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17.2: Acids, Bases, and Salts

Learning Objectives

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Write chemical reactions between an Arrhenius acid and an Arrhenius base and between Brønsted-Lowry acid and a Brønsted-Lowry base.

There are three major classifications of substances known as acids or bases. The Arrhenius definition states that an acid produces H^+ in solution and a base produces OH^-. This theory was developed by Svante Arrhenius in 1883. Later, two more sophisticated and general theories were proposed. These are the Brønsted-Lowry and the Lewis definitions of acids and bases. The Lewis theory is discussed elsewhere.

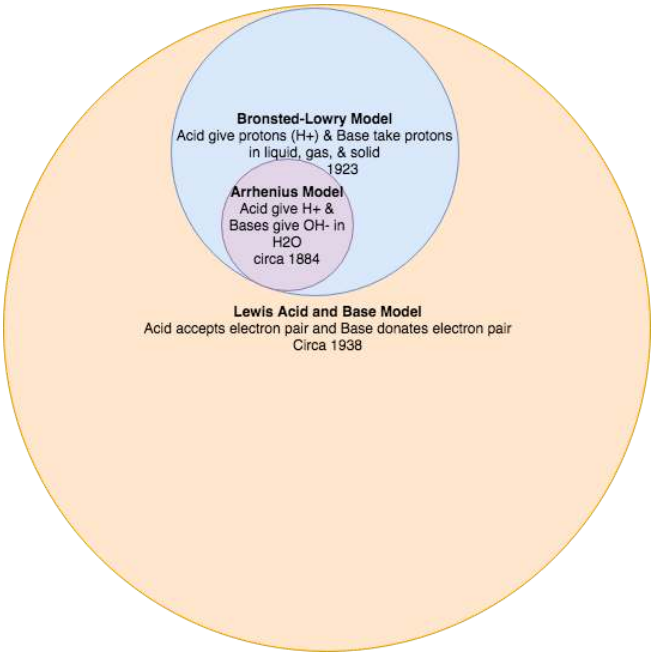


Figure **17.2.1** Acid base reaction theories as superset and subset models.

The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that **increases the concentration of H^+ ions** that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

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

In this reaction, hydrochloric acid (***HCl***) dissociates completely into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

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

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

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

In this reaction, sodium hydroxide (NaOH) disassociates into sodium (***Na^+***) and hydroxide (***OH^-***) ions when dissolved in water, thereby releasing OH^- ions into solution.

> *Arrhenius acids are substances which produce hydrogen ions in solution and Arrhenius bases are substances which produce hydroxide ions in solution.*

Limitations to the Arrhenius Theory

The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia (NH_3), which in the presence of water, releases hydroxide ions into solution, but does not contain OH- itself. Also, the Arrhenius definition of acid and base is limited to aqueous (i.e., water) solutions.

The Brønsted-Lowry Theory of Acids and Bases

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, **a Brønsted-Lowry acid** is a **proton donor (PD)**, while **a Brønsted-Lowry base** is a **proton acceptor (PA)**.

> *A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.*

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$\mathrm{NH_3\,(aq) + H_2O\,(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \tag{17.2.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows (Figure **17.2.2**):

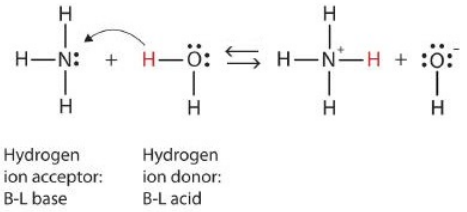


Figure **17.2.2** reaction of ammonia and water.

Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

The Hydronium Ion

A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $\mathbf{H_5O_2^+}$ or $\mathbf{H_9O_4^+}$ rather than $\mathbf{H_3O^+}$. It is simpler, however, to use $\mathbf{H_3O^+}$ to represent the hydronium ion.

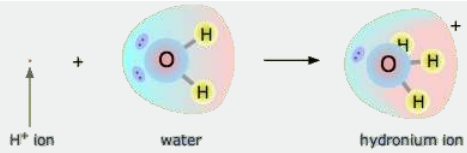


Figure **17.2.3** reaction of hydrogen and water to form hydronium. (CC BY-NC 3.0

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$\mathbf{HCl\,(g) + H_2O\ (\ell)\ \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)} \tag{17.2.2}$$

We can depict this process using Lewis electron dot diagrams (Figure **17.2.4**):

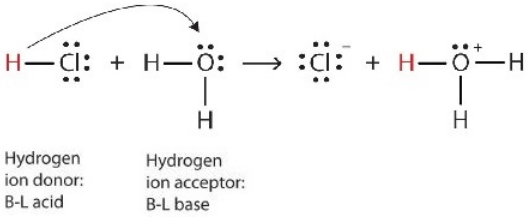


Figure **17.2.4** Lewis electron dot diagram of HCl dissolved in H_2O

Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor, H_2O is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

A summary of the acid-base definitions based on the Arrhenius and Bronstes-Lowry theories is given in Table **17.2.1**.

***Table* 17.2.1** *Acid-Base Definitions*

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

All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Example 17.2.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

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

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise 17.2.1

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

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

Answer

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

Exercise 17.2.2

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer:

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

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

Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

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

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) $\mathbf{HPO_4^{2-}}$.**

Summary

- An Arrhenius acid is a compound that increases the H^+ ion concentration and an Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
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17.3: Acidic and Basic Anhydrides

Learning Objectives

- Identify acid anyhdrides and basic anhydrides.
- Know the reactions of acid and basic anhydrides with water.

Metal oxides are substances used in the manufacture of commonly used bases like calcium hydroxide (traditionally known as slaked lime), sodium hydroxide and potassium hydroxide. Acid anhydrides (non-metal oxides) are environmentally relevant. Sulfur and nitrogen oxides are considered air pollutants as they react with atmospheric water vapor to produce acid rain (Chapter 13).

Nonmetal Oxides: Acid Anhydrides

Acid anhydrides are compounds that turn into an acid when you add water. They are non-metal oxides. The oxides of period three elements demonstrate periodicity with respect to acidity. As you move across the period, the oxides become more acidic. Sodium and magnesium oxides are alkaline. Aluminium oxides are amphoteric (reacting both as a base or acid). Silicon, phosphorus, sulfur, and chlorine oxides are acidic. Some non-metal oxides, such as nitrous oxide (N_2O) and carbon monoxide (CO), do not display any acid/base characteristics. These are a little more complicated than basic anhydrides, so don't worry too much about them right now.

Several examples of reactions involving nonmetal oxides are as follows:

1. Carbon dioxide is the anhydride of carbonic acid:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3\,(aq)$$

2. Sulfur dioxide reacts with water to form the weak acid, sulfurous acid:

$$SO_2(g) + H_2O\,(l) \rightarrow H_2SO_3\,(aq)$$

3. Sulfur trioxide forms the strong sulfuric acid with water (so, sulfur trioxide is the anhydride of sulfuric acid):

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4\,(aq)$$

This reaction is important in the manufacture of the acid.

Metal Oxides: Basic Anhydrides

Oxides of more electropositive elements like the alkali or alkaline earth metals tend to be basic. They are called *basic anhydrides*. Exposed to water, they may form bases (basic hydroxides). Sodium oxide is basic—when hydrated, it forms sodium hydroxide. Here's another example:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2\,(aq)$$

If the metal is an alkali or alkaline earth, the reaction probably happens quickly and produces a lot of heat. If the metal is a transition metal, the reaction might not happen so easily or at all.

Summary

- Acid anhydrides are nonmetal oxides that react with water to form acids.
- Basic anhydrides are metal oxides that react with water to form bases.

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17.4: Strong and Weak Acids and Bases

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.

Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in H_2O, it completely dissociates into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

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

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

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

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

As it turns out, there are very few strong acids, which are given in Table **17.4.1**. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

> *Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.*

Table **17.4.1** Strong Acids and Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table **17.4.1**); any base not listed is a weak base. All strong bases are OH^- compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

Example 17.4.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. C_5H_5N

Solution

a. Because HCl is listed in Table **17.4.1**, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table **17.4.1**, it is a strong base.
c. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 17.4.1

Identify each acid or base as strong or weak.

a. **RbOH**
b. **HNO_2**

Answer a

strong base

Answer b

weak acid

Example 17.4.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

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

Because $Ca(OH)_2$ is listed in Table **17.4.1**, this reaction proceeds 100% to products.

Exercise 17.4.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer a

The reaction is as follows:

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

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

Summary

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

Contributors and Attributions

- Libretext: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

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17.5: Neutralization

Learning Objective

- Write acid-base neutralization reactions.

What happens when an acid such as HCl is mixed with a base such as NaOH:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

When an acid and a base are combined, water and a salt are the products. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$\mathrm{H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)}$$

Removing the spectator ions we get the net ionic equation:

$$\mathrm{H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l)}$$

When a strong acid and a strong base are combined in the proper amounts - when $[\mathrm{H^+}]$ equals $[\mathrm{OH^-}]$\) - a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. We will not go into details here, but generally if a strong acid is mixed with a weak base there the resulting solution will be slightly acidic; if a strong base is mixed with a weak acid the solution will be slightly basic.

Neutralization



***Video* 17.5.1** *Acid-base neutralization reaction.*

Example 17.5.1: propionic acid + calcium hydroxide

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].

Solution

Example **17.5.1**: steps for problem solving the reaction of propionic acid + calcium hydroxide

Steps	Reaction
Write the unbalanced equation. This is a double displacement reaction, so the cations and anions swap to create the water and the salt.	$CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$
Balance the equation. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$ to provide H^+ ions.	$\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$

? Exercise 17.5.1

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

Answer

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

Applications

In analytical laboratories, chemical methods are used for determining the amounts of acids or bases in foods and household and industrial chemicals.

In , chemical neutralization methods are often applied to reduce the damage that an effluent may cause upon release to the environment.

There are many uses of neutralization reactions that are acid-alkali reactions. A very common use is antacid tablets (section 7.8).

In chemical synthesis of nanomaterials, the heat of neutralization reaction can be used to facilitate the chemical reduction of metal precursors.

Also in the digestive tract, neutralization reactions are used when food is moved from the stomach to the intestines. In order for the nutrients to be absorbed through the intestinal wall, an alkaline environment is needed, so the pancreas produce an antacid bicarbonate to cause this transformation to occur.

Another common use, though perhaps not as widely known, is in fertilizers and control of soil pH. Slaked lime (calcium hydroxide) or limestone (calcium carbonate) may be worked into soil that is too acidic for plant growth. Fertilizers that improve plant growth are made by neutralizing sulfuric acid (H_2SO_4) or nitric acid (HNO_3) with ammonia gas (NH_3), making or . These are salts utilized in the fertilizer.

Industrially, a by-product of the burning of coal, gas, may combine with water vapor in the air to eventually produce sulfuric acid, which falls as acid rain. To prevent the sulfur dioxide from being released, a device known as a scrubber gleans the gas from smoke stacks. This device first blows calcium carbonate into the combustion chamber where it decomposes into calcium oxide (lime) and carbon dioxide. This lime then reacts with the sulfur dioxide produced forming calcium sulfite. A suspension of lime is then injected into the mixture to produce a slurry, which removes the and any remaining unreacted sulfur dioxide.

Fluffy Cakes

Q: How do acid-base reactions make cake fluffy?



Figure 17.5.1 Cake with buttercream frosting. Image use with permission (Public domain; Scheinwerfermann)..png

A: Usually cakes include an acidic ingredient (this varies) and sodium bicarbonate, a base. When they react, the proton from the acid is transferred to the bicarbonate, making the weak acid carbonic acid. Carbonic acid is the product of an acid anhydride reaction between carbon dioxide and water. This reaction can be reversed, or carbonic acid can decompose into water and carbon dioxide. Especially at the high temperatures inside a baking cake, this decomposition will happen, and produce carbon dioxide gas. The pressure of the hot gas will form bubbles inside the cake, making it fluffy.

Summary

- Acids and bases combine and produce salt and water.

Contributors and Attributions

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

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17.6: The pH Scale

Learning Objectives

- Define ***pH***.
- Determine the pH of acidic and basic solutions.
- Determine the hydrogen (hydronium) ion concentration from pH and vice versa.

Molar concentration values of hydrogen [H^+] can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions. This is known as the ***pH*** scale. The range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use ***pH*** to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the [H^+] as a solution with a pH of 2.0, which in turn has 10 times the [H^+] as a solution with a pH of 3.0 and so forth.

Warning: The pH scale has no limits

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on [$H+$], we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.



Figure **17.6.1** The pH scale.

Figure **17.6.2** illustrates the relationship between pH and the hydrogen ion concentration, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** [H^+], which will give a positive value for pH.

The general formula for determining [H^+] from pH is as follows:

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

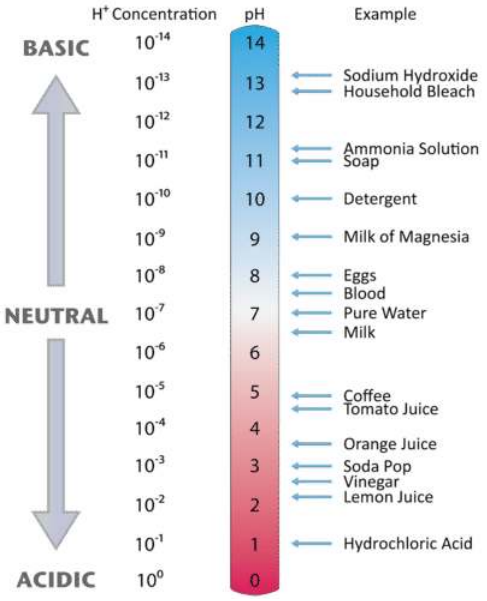


Figure **17.6.2** The ***pH*** values for several common materials with corresponding hydrogen ion concentration, [H+] .

Example 17.6.1

Label each solution as acidic, basic, or neutral based only on the stated ***pH***.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Answer

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

Exercise 17.6.1

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

a. human blood with ***pH*** = 7.4
b. household ammonia with ***pH*** = 11.0
c. cherries with ***pH*** = 3.6

Answer a

basic

Answer b

basic

Answer c

acidic

Table **17.6.1**: gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

Table **17.6.1** Typical pH Values of Various Substances*

Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0
*Actual values may vary depending on conditions	

Example 17.6.2:

What is the $[H^+]$ for an aqueous solution whose pH is 6?

Solution

The pH value of 6 denotes that the exponent of 10 is -6. Therefore the answer is

$$[H^+] = 1.0 \times 10^{-6} M$$

Exercise 17.6.2

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

Answer

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

Example 17.6.3:

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0×10^{-7}M? Is the solution acidic, basic, or neutral.

Solution

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

Exercise 17.6.3

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0×10^{-3}M? Is the solution acidic, basic, or neutral.

Solution

The hydrogen ion concentration is 1.0 x 10^{-3}M. The exponent of 10 is -3, which denoted that pH= -(-3) = **3**. The solution is **acidic**.

Summary

To make pH even easier to work with, pH is defined as the ***negative*** **log of** [H^+], which will give a positive value for pH.

pH is usually (but not always) between 0 and 14.

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

Contributors and Attributions

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

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17.7: Buffers and Conjugate Acid-Base Pairs

Learning Objectives

- Identify conjugate acid base pair.
- Define buffers and know the composition of different buffer systems.
- Describe how buffers work.

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, $\mathbf{OH^-}$, and the conjugate acid of ammonia, $\mathbf{NH_4^+}$:

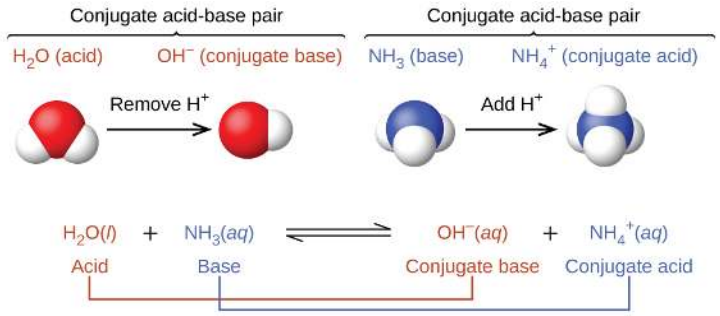


Figure **17.7.2**.This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $\boldsymbol{NH_4^+/NH_3}$ and $\boldsymbol{H_2O/OH^-}$.

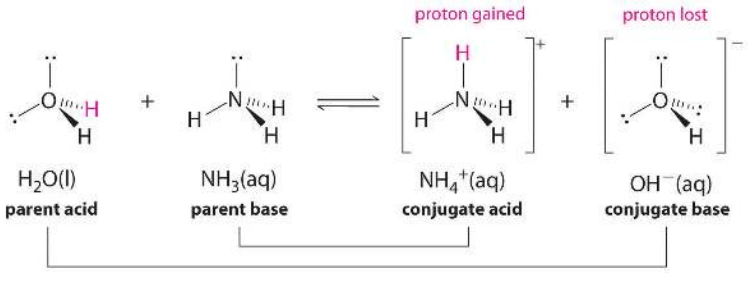


Figure **17.7.2**. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid

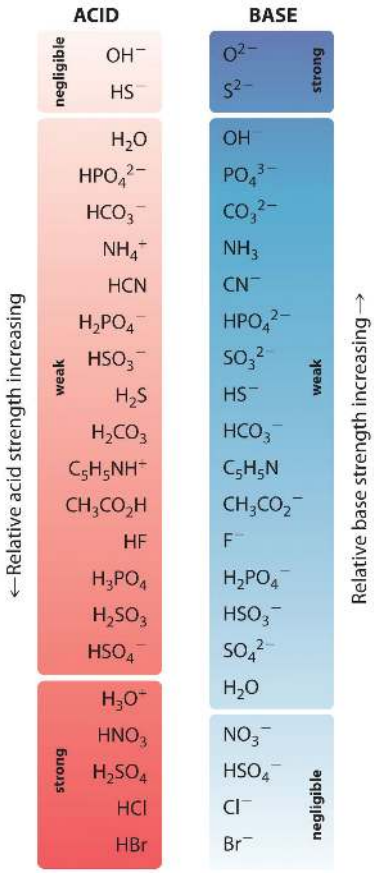


Figure **17.7.3** The Relative Strengths of Some Common Conjugate Acid–Base Pairs

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

Example 17.7.1

Identify the conjugate acid-base pairs in this equilibrium.

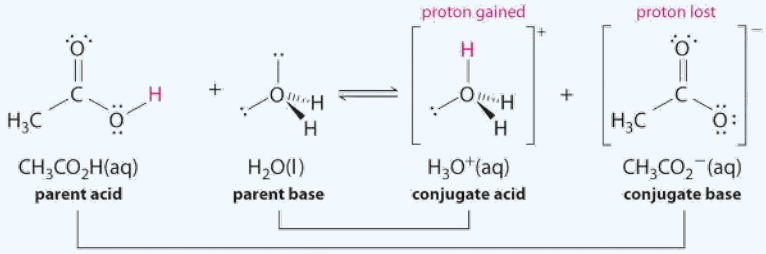
$$\mathbf{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, $\boldsymbol{H_3O^+}$ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid–base pairs:

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



Example **17.7.1** the reaction of acetic acid with water

Example 17.7.2

Identify the conjugate acid-base pairs in this equilibrium.

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

Solution

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

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

Exercise 17.7.1

Identify the conjugate acid-base pairs in this equilibrium.

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

Answer:

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

Buffer Solutions

Weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of H^+ or OH^- ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

This mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid, or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing NH_3 (a weak base) and NH_4Cl (a salt derived from that weak base).

Let us use an $HC_2H_3O_2/NaC_2H_3O_2$ buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those OH^- ions will react with the $HC_2H_3O_2$ in an acid-base reaction:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \qquad (17.7.1)$$

Rather than changing the pH dramatically by making the solution basic, the added OH^- ions react to make H_2O, so the pH does not change much.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of H^+ ions and $C_2H_3O_2^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) \qquad (17.7.2)$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure **17.7.2** illustrates both actions of a buffer.

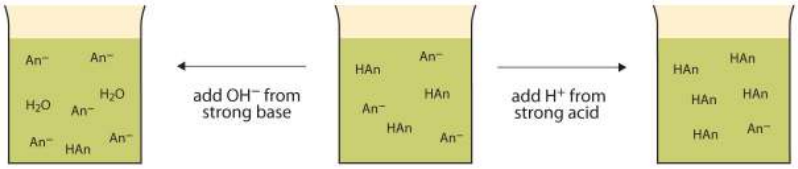


Figure **17.7.4** The actions of buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, NH_3 molecules can react with any excess H^+ ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

while the $NH_4^+(aq)$ ion can react with any OH^- ions introduced by strong bases:

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

Some common buffer systems are listed in the table below.

Table **17.7.1** Some Common Buffers

Table **17.7.1** *Some Common Buffers*

Buffer System	Buffer Components	pH of buffer (equal molarities of both components)
Acetic acid/acetate ion	CH_3COOH/CH_3COO^-	4.74
Carbonic acid/hydrogen carbonate ion	H_2CO_3/HCO_3^-	6.38
Dihydrogen phosphate ion/hydrogen phosphate ion	$H_2PO_4^-/HPO_4^{2-}$	7.21
Ammonia/ammonium ion	NH_3/NH_4^+	9.25

Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Example 17.7.3:

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [CHO_2^-]). The combination of these two solutes would make a buffer solution.
2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.

3. CH_3NH_2 is methylamine, which is like NH_3 with one of its H atoms substituted with a CH_3 group. Because it is not listed in Table **17.7.1**, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. NH_3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 17.7.2

Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Answer a

Yes.

Answer b

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

Answer c

Yes.

Answer d

No. Need a weak base or acid.

Food and Drink Application: the Acid that Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table **17.7.1**, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

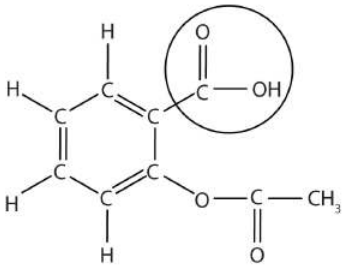


Figure **17.7.5**: The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent—usually MgO—that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects—gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver

problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin will remain on the market.

Summary

- A buffer is a solution that resists sudden changes in pH.
- Reactions showing how buffers regulate pH are described.

Contributors and Attributions

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17.8: Acids and Bases in Industry and in Daily Life

Learning Objective

- Know the many uses of common acids and bases.

Antacids: A Basic Remedy

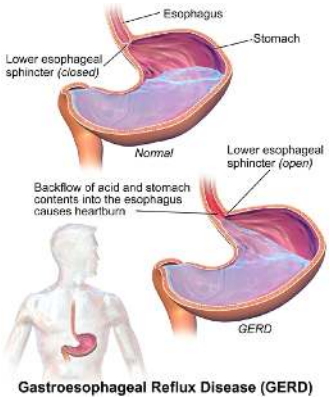


Figure **17.8.1**. Antacids are available over the counter and are taken by mouth to quickly relieve occasional heartburn, the major symptom of gastroesophageal reflux disease and also indigestion. Treatment with antacids alone is symptomatic and only justified for minor symptoms.

Antacids contain alkaline ions that chemically neutralize stomach gastric acid, reducing damage and relieving pain. For example, Tums is a very commonly used antacid that can be bought over the counter. Other antacids, such as Alka Seltzer, work in similar ways. Below, show the mechanism and products for reaction in which calcium carbonate (the active ingredient in Tums) neutralizes HCl in a simple proton transfer reaction.

$$CaCO_3\,(s) + HCl\,(aq) \rightarrow H_2CO_3\,(aq) + CaCl_2\,(aq)$$

Following this acid-base reaction, carbonic acid quickly degrades into CO_2 and H_2O.

$$H_2CO_3\,(aq) \rightarrow CO_2(g) + H_2O(l)$$

***Figure* 17.8.1** *A comparison of a healthy condition to GERD. I*

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Under the generic name algeldrate, aluminium hydroxide is used as an antacid. Aluminium hydroxide is preferred over other alternatives such as sodium bicarbonate because $Al(OH)_3$, being insoluble, does not increase the pH of stomach above 7 and hence, does not trigger secretion of excess stomach acid. Brand names include Alu-Cap, Aludrox, Gaviscon, and Pepsamar. In 2016 Gaviscon was one of the biggest selling branded over-the-counter medications sold in Great Britain, with sales of £62 million. It reacts with excess acid in the stomach, reducing the acidity of the stomach content, which may relieve the symptoms of ulcers, heartburn or dyspepsia. Such products can cause constipation, because the aluminum ions inhibit the contractions of smooth muscle cells in the gastrointestinal tract, slowing peristalsis and lengthening the time needed for stool to pass through the colon. Some such products are formulated to minimize such effects through the inclusion of equal concentrations of magnesium hydroxide or magnesium carbonate, which have counterbalancing laxative effects.

Antacids are distinct from acid-reducing drugs like H_2-receptor antagonists or proton pump inhibitors and they do not kill the bacteria *Helicobacter pylori*, which causes most ulcers. Ranitidine (Zantac), famotidine (Pepcid AC), and cimetidine (Tagamet) are in a class of medications called H_2 blockers. It decreases the amount of acid made in the stomach and are used to treat ulcers; gastroesophageal reflux disease (GERD), a condition in which backward flow of acid from the stomach causes heartburn and injury of the food pipe (esophagus); and conditions where the stomach produces too much acid, such as Zollinger-Ellison syndrome. These over-the-counter medications are used to prevent and treat symptoms of heartburn associated with acid indigestion and sour

stomach. Omeprazole (Prilosec) also works by decreasing the amount of acid made in the stomach and is in a class of medications called proton-pump inhibitors.

Acids and Bases in Industry and at Home

Common Acids

It should not be hard for you to name several common acids, but you might find that listing bases is just a little more difficult. Here's a partial list of some common acids, along with some chemical formulas:

Table **17.8.1** Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the "fiz" in carbonated drinks	As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. One of the most important applications of hydrochloric acid is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing. Another major use of hydrochloric acid is in the production of organic compounds, such as vinyl chloride and dichloroethane for PVC. Other organic compounds produced with hydrochloric acid include bisphenol A for polycarbonate, activated carbon, and ascorbic acid, as well as numerous pharmaceutical products. Other inorganic compounds produced with hydrochloric acid include road application salt calcium chloride, nickel(II) chloride for electroplating, and zinc chloride for the galvanizing industry and battery production.

Sulfuric Acid

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. World production in the year 2004 was about 180 million tonnes, with the following geographic distribution: Asia 35%, North America (including Mexico) 24%, Africa 11%, Western Europe 10%, Eastern Europe and Russia 10%, Australia and Oceania 7%, South America 7%. Most of this amount (≈60%) is consumed for fertilizers, particularly superphosphates, ammonium phosphate and ammonium sulfates. About 20% is used in chemical industry for production of detergents, synthetic resins, dyestuffs, pharmaceuticals, petroleum catalysts, insecticides and antifreeze, as well as in various processes such as oil well acidicizing, aluminium reduction, paper sizing, water treatment. About 6% of uses are related to pigments and include paints, enamels, printing inks, coated fabrics and paper, and the rest is dispersed into a multitude of applications such as production of explosives, cellophane, acetate and viscose textiles, lubricants, non-ferrous metals, and batteries.



Figure **17.8.2**: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

Because the hydration of sulfuric acid is thermodynamically favorable (and is highly exothermic) and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating property, removing water ($\mathbf{H_2O}$) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation ???).

Nitric Acid

Nitric acid ($\mathbf{HNO_3}$) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. The main industrial use of nitric acid is for the production of fertilizers. Nitric acid is neutralized with ammonia to give ammonium nitrate. This application consumes 75–80% of the 26 million tonnes produced annually (1987). The other main applications are for the production of explosives, nylon precursors, and specialty organic compounds.



Figure **17.8.3**: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Table **17.8.2** *Common Bases and Its Uses*

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula $\mathbf{NaOH}$.

It is a popular strong base used in industry. Around 56% of sodium hydroxide produced is used by industry, 25% of which is used in the paper industry. Sodium hydroxide is also used in the manufacture of sodium salts and detergents, pH regulation, and organic synthesis. It is used in the Bayer process of aluminium production. In bulk, it is most often handled as an aqueous solution, since solutions are cheaper and easier to handle.

Sodium hydroxide is used in many scenarios where it is desirable to increase the alkalinity of a mixture, or to neutralize acids.



Figure **17.8.4** Sample of sodium hydroxide as pellets in a watchglass. (Public Domain; Walkerma).

Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathbf{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime.

One significant application of calcium hydroxide is as a flocculant, in water and sewage treatment. It is also used in fresh water treatment for raising the pH of the water so that pipes will not corrode where the base water is acidic, because it is self-regulating and does not raise the pH too much.

It is also used in the preparation of ammonia gas (NH_3), using the following reaction:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

Another large application is in the paper industry, where it is an intermediate in the reaction in the production of sodium hydroxide. Because of its low toxicity and the mildness of its basic properties, slaked lime is widely used in the food industry:

Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula $\mathbf{NH_3}$ and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

Globally, approximately 88% (as of 2014) of ammonia is used as fertilizers either as its salts, solutions or anhydrously. When applied to soil, it helps provide increased yields of crops such as maize and wheat. 30% of agricultural nitrogen applied in the US is in the form of anhydrous ammonia and worldwide 110 million tonnes are applied each year. Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

Common acids and bases have many and various uses in industry and in daily life.

Contributors and Attributions

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17.9: Acid Rain- Air Pollution Water Pollution

Learning Objective

- Describe acid rain and its effects.

Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere (Figure **17.9.1**) containing higher than normal amounts of nitric and sulfuric acids. The precursors, or chemical forerunners, of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid.

$$SO_2 + HOH \rightarrow H_2SO_3 \tag{17.9.1}$$

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3 \tag{17.9.2}$$

When sulfur dioxide and nitrogen oxides are released from power plants and other sources, *prevailing winds* blow these compounds across state and national borders, sometimes over hundreds of miles.

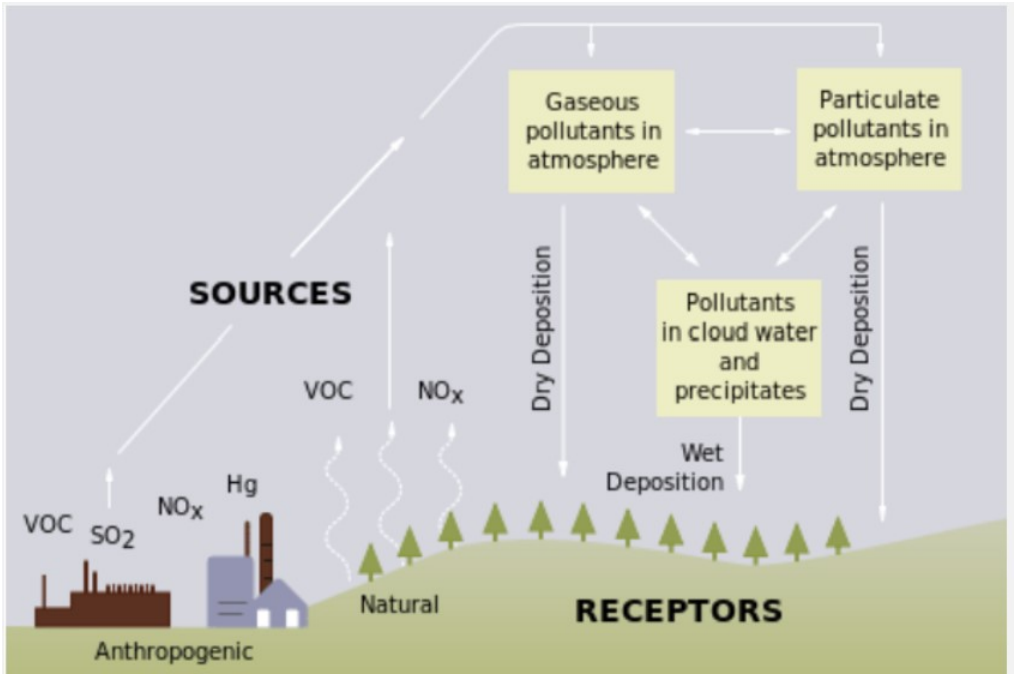


Figure **17.9.1** Processes involved in acid deposition.

Acid rain is measured using a scale called “pH.” The lower a substance’s pH, the more acidic it is. Pure water has a pH of 7.0. However, normal rain is slightly acidic because carbon dioxide (CO_2) dissolves into it forming weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2. As of 2000, the most acidic rain falling in the U.S. has a pH of about 4.3.

Effects of Acid Rain

Acid rain causes **acidification** of lakes and streams and contributes to the damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation’s cultural heritage. Prior to falling to the earth, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and their particulate matter derivatives—sulfates and nitrates—contribute to visibility degradation and harm public health.

The **ecological** effects of acid rain are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid rain. Acid rain primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called “buffering capacity”). Lakes and streams become acidic (i.e., the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms. Acid rain causes slower growth, injury, or death of forests as shown in Figure **17.9.2**. Of course, acid rain is not the only cause of such conditions. Other factors contribute to the overall stress of these areas, including air pollutants, insects, disease, drought, or very cold weather. In most cases, in fact, the impacts of acid rain on trees are due to the combined effects of acid rain and these other environmental stressors.



Figure **17.9.2**. Acid rain damage to a forest in the Czech Republic.

Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze).

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate ($CaCO_3$), a salt derived from the weak acid H_2CO_3. The reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + H_2O_{(l)} + CO_{2(g)} \tag{17.9.3}$$

Because $CaSO_4$ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone.

These effects significantly reduce the societal value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars (Figure **17.9.3**).



Figure **17.9.3**. A gargoyle that has been damaged by acid rain.

Sulfates and nitrates that form in the atmosphere from sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions contribute to **visibility impairment,** meaning we cannot see as far or as clearly through the air. The pollutants that cause acid rain—sulfur dioxide (SO_2) and nitrogen oxides (NO_x)—damage **human health**. These gases interact in the atmosphere to form fine sulfate and nitrate particles that can be transported long distances by winds and inhaled deep into people's lungs. Fine particles can also penetrate indoors. Many scientific studies have identified a relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis.

Summary

- Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids.
- Acidic rain water in the soil, streams, lakes, and marshes (and other bodies of water) can be harmful to trees, plants, animals, especially aquatic plants and animals.
- Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze) and the deterioration of paint and stone (such as marble and limestone).

Contributors and Attributions

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17.10: All-Purpose and Special Purpose Cleaning Products

Learning Objective

- List various cleaners and their modes of action.

Cleaning agents or **hard-surface cleaners** are substances (usually liquids, powders, sprays, or granules) used to remove dirt, including dust, stains, bad smells, and clutter on surfaces. Purposes of cleaning agents include health, beauty, removing offensive odor, and avoiding the spread of dirt and contaminants to oneself and others. Some cleaning agents can kill bacteria (e.g. door handle bacteria, as well as bacteria on worktops and other metallic surfaces) and clean at the same time. Others, called degreasers, contain organic solvents to help dissolve oils and fats.

Acidic cleaning agents are mainly used for removal of inorganic deposits like scaling. The active ingredients are normally strong mineral acids and chelants. Often, surfactants and corrosion inhibitors are added to the acid.

Hydrochloric acid is a common mineral acid typically used for concrete. Vinegar can also be used to clean hard surfaces and remove calcium deposits that also helps to maintain our environment bacteria free. Sulphuric acid is used in acidic drain cleaners to unblock clogged pipes by dissolving greases, proteins, and even carbohydrate-containing substances such as toilet tissue.

Alkaline cleaning agents contain strong bases like sodium hydroxide or potassium hydroxide. Bleach (pH 12) and ammonia (pH 11) are common alkaline cleaning agents. Often, dispersants, to prevent redeposition of dissolved dirt, and chelants, to attack rust, are added to the alkaline agent.

Alkaline cleaners can dissolve fats (including grease), oils, and protein-based substances.

Neutral washing agents are pH-neutral and based on non-ionic surfactants that disperse different types.

Scouring agents are mixtures of the usual cleaning chemicals (surfactants, water softeners) as well as abrasive powders. The abrasive powder must be of a uniform particle size.

Particles are usually smaller than 0.05 mm. Pumice, calcium carbonate (limestone, chalk, dolomite), kaolinite, quartz, soapstone or talc are often used as abrasives, i.e. polishing agents.

Special bleaching powders contain compounds that release sodium hypochlorite, the classical household bleaching agent. These precursor agents include trichloroisocyanuric acid and mixtures of sodium hypochlorite ("chlorinated orthophosphate").

Examples of notable products include: Ajax, Bar Keepers Friend, Bon Ami, Comet, Vim, Zud, and others.

All-Purpose Cleaners

All-purpose cleansers (Figure **17.10.1**) contain mixtures of anionic and nonionic surfactants, polymeric phosphates or other sequestering agents, solvents, hydrotropic substances, polymeric compounds, corrosion inhibitors, skin-protective agents, and sometimes perfumes and colorants.[7] Aversive agents, such as denatonium, are occasionally added to cleaning products to discourage animals and small children from consuming them.



Figure **17.10.1** *Fabuloso multipurpose cleaner and generic surface cleaners. Source: Wikipedia*

Some cleaners contain water-soluble organic solvents like glycol ethers and fatty alcohols, which ease the removal of oil, fat and paint. Disinfectant additives include quaternary ammonium compounds, phenol derivatives, terpene alcohols (pine oil), aldehydes, and aldehyde-amine condensation products.

All-purpose cleaners are usually concentrated solutions of surfactants and water softeners, which enhance the behavior of surfactant in hard water. Typical surfactants are alkylbenzenesulfonates, an anionic detergent, and modified fatty alcohols. A typical water softener is sodium triphosphate.

All-purpose cleansers are effective with most common kinds of dirt. Their dilute solutions are neutral or weakly alkaline, and are safe for use on most surfaces.

Special Purpose Cleaners

Traditional **oven cleaners** contain sodium hydroxide (lye), solvents, and other ingredients,[3][4][5] and work best when used in a slightly-warm (not hot) oven. If used in a self-cleaning oven, the lye will cause permanent damage to the oven.

New-style oven cleaners are based on ingredients other than lye. These products must be used in a cold oven. Most new-style oven cleaners can be used in self-cleaning ovens.

Oven cleaners are some of the most toxic household cleaning products available on the market.[6] Correct use of an oven cleaner may be reasonably safe, but incorrect use can have harmful effects.

One popular oven cleaner brand in the US is "Easy-Off", sold by Reckitt Benckiser. Popular choices in the UK include "Zep Oven Brite" and "Mr Muscle Oven Cleaner".

Toilet bowl cleaning agents often are aimed at removal of calcium carbonate deposits, which are attacked by acids. Powdered cleaners contain acids that come in the form of solid salts, such as sodium hydrogen sulfate. Liquid toilet bowl cleaners contain other acids, typically dilute hydrochloric, phosphoric, or formic acids. These convert the calcium carbonate into salts that are soluble in water or are easily rinsed away.

Chemical drain cleaners can be in solid or liquid form that are readily available through hardware stores, though some (primarily acidic ones) are intended for use by licensed plumbers.[1]Alkaline drain cleaners are available in either solid or liquid state while the acidic ones are usually in liquid form.



Figure **17.10.2** *Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. Source: Wikipedia*

Metal cleaners are used for cleaning stainless steel sinks, faucets, metal trim, silverware, etc. These products contain abrasives (e.g., siliceous chalk, diatomaceous earth, alumina) with a particle size < 20 μm. Fatty alcohol or alkylphenol polyglycol ethers with 7-12 ethylene oxide (EO) units are used as surfactants.[7]

For ferrous metals, the cleaners contain chelating agents, abrasives, and surfactants. These agents include citric and phosphoric acids, which are nonaggressive. Surfactants are usually modified fatty alcohols. Silver cleaning is a specialty since silver is noble but tends to tarnish via formation of black silver sulfide, which is removable via silver-specific complexants such as thiourea.

Stainless steel, nickel, and chromium cleaners contain lactic, citric, or phosphoric acid. A solvent (mineral spirits) may be added.

Nonferrous metal cleaners contain ammonia, ammonium soaps (ammonium oleate, stearate) and chelating agents (ammonium citrate, oxalate).

For special type of precious metals especially those used for luxury watches and high-end jewelry, special type of cleaning agents are usually used to clean and protect them from the elements.

Glass cleaners. Light duty hard surface cleaners are not intended to handle heavy dirt and grease. Because these products are expected to clean without rinsing and result in a streak-free shine, they contain no salts. Typical window cleaning items consist of alcohols, either ethanol or isopropanol, and surfactants for dissolving grease. Other components include small amounts of ammonia as well as dyes and perfumes.

These are composed of organic,water-miscible solvent such as isopropyl alcohol and an alkaline detergent. Some glass cleaners also contain a fine, mild abrasive. Most glass cleaners are available as sprays or liquid. They are sprayed directly onto windows, mirrors and other glass surfaces or applied on with a soft cloth and rubbed off using a soft ,lint-free duster. A glass cloth ideal for the purpose and soft water to which some methylated spirit or vinegar is added which is an inexpensive glass cleaner.

Silverware can be freed of silver sulfide tarnish with thiourea, and either hydrochloric or sulfuric acid.

Building facade cleaners. For acid-resistant building facades, such as brick, acids are typically used. These include mixtures of phosphoric and hydrofluoric acids as well as surfactants. For acid-sensitive facades such as concrete, strongly alkaline cleaners are used such as sodium hydroxide and thickeners. Both types of cleaners require a rinsing and often special care since the solutions are aggressive toward skin.

Drain Cleaners: Danger and Usage Considerations

Danger arises from chemical drain cleaners' potential to injure eyes, lungs, and skin; and damage to clothing and household materials such as wood, paint, aluminum, and fiberglass. Chemical drain cleaners should be used only according to the manufacturer's instructions, as other use may cause injury.[7] Strongly corrosive and acid drain cleaners are among the most hazardous household products available to the public. Chemical drain cleaners can cause strong reactions—sometimes explosively—with other chemicals that may have been used previously, which can result in serious injury to anyone in the vicinity.[8] In one such incident, a five-year-old boy was left scarred for life after an acidic drain cleaner leaked through his bedroom ceiling as he slept.[9]

Strong Alkali Drain cleaners are equally capable of causing rapid, severe burns, as seen in the cases of a woman doused with concentrated lye in an attack. A small girl was also permanently disfigured by a common lye drain opener.,[10][11] Moreover, because the acidic or basic drain cleaners themselves are washed down the drain, this contributes to pollution in the water supply. The heat generation can also soften plastic PVC pipes, and the pressure buildup by gas generation can cause older pipes to burst. Commercial chemical based solutions can cause corrosion and other damage to your pipes and sewer lines[12]

Oftentimes, individuals may unknowingly mix two different types of drain cleaners, which can even lead to deadly results. For example, consider the mixing of an acidic and basic drain cleaner:

Sulfuric Acid + Sodium Hydroxide → sodium sulfate (a salt) + water

$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2H_2O$

The neutralization reaction of the acid and base may seem harmless, but in reality this reaction is extremely exothermic and can cause pipes to violently explode. Consider another example of mixing, this time between an acid drain cleaner and bleach:

Hydrochloric acid + bleach → water + table salt + chlorine gas

$2HCl + NaClO \rightarrow H_2O + NaCl + Cl_2$

This reaction generates chlorine gas, which is toxic to the lungs.

Green Cleaners

Green cleaning refers to using cleaning methods and products with environmentally friendly ingredients and procedures which are designed to preserve human health and environmental quality.[1] Green cleaning techniques and products avoid the use of products which contain toxic chemicals, some of which emit volatile organic compounds causing respiratory, dermatological and other conditions.[2] Green cleaning can also describe the way residential and industrial cleaning products are manufactured, packaged and distributed. If the manufacturing process is environmentally friendly and the products are biodegradable, then the term "*green*" or "*eco-friendly*" may apply.

Common household ingredients that are safe to use on its own or in combination for a variety of cleaning applications include baking soda, soap, alcohol, cornstarch, lemon juice, white vinegar, citrus solvent, washing soda (SAL soda or sodium carbonate), oxygen bleach, vegetable oil, and hydrogen peroxide.

WEB LINK

The links below provide information on safe ingredients for homemade substitutions and homemade cleaning products.

https://learn.eartheasy.com/guides/non-toxic-home-cleaning/#homecleaning

Summary

- All-purpose cleansers are effective with most common kinds of dirt and are formulated to contain mixtures of surfactants, sequestering agents, solvents, hydrotropic substances, polymeric compounds, corrosion inhibitors, skin-protective agents, and sometimes perfumes and colorants.
- Special purpose cleaners are formulated with specific chemicals to effectively remove dirt, grime or stain from a particular surface (e.g. glass cleaner, metal cleaner, etc.) or appliance (e.g. oven cleaner).
- Green cleaners are gaining popularity among environmentalists who are interested in using cleaners that are made of biodegradable and eco-friendly ingredients.

Contributors

- Wikipedia
- Cowan, Shannon. “Non-Toxic Home Cleaning.” *Eartheasy Guides & Articles*, learn.eartheasy.com/guides/non-toxic-home-cleaning/.
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CHAPTER OVERVIEW

18: Organic Chemistry

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{18.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.



Figure **18.1** *All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)*

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **18.1**.

Table 18.1: 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 **18.1** 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 **18.1**.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

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- 18.1: Prelude to Organic Chemistry
  18.2: Aliphatic Hydrocarbons
  18.3: Aromatic Compounds- Benzene and Its Relatives
  18.4: Halogenated Hydrocarbons- Many Uses, Some Hazards
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18.1: Prelude to Organic Chemistry

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{18.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.



Figure **18.1.1** All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by "annszyp"/Wikimedia Commons; credit right: modification of work by George Shuklin)

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **18.1.1**.

Table **18.1.1**: 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 **18.1.1** 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 **18.1.1**.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

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18.2: Aliphatic Hydrocarbons

Learning Objectives

- Define and identify alkanes, alkenes, alkynes, and cyclic hydrocarbons.
- List some properties of hydrocarbons.
- Identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- Define structural and geometric isomers.
- Write condensed structural formulas and draw line-angle formulas given complete structural formulas for alkanes,alkenes, alkynes, and cyclic hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. **Aliphatic hydrocarbons** are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and a**lkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called ***cycloalkanes*** (or *cycloalkenes* or *cycloalkynes*). Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Note

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

Alkanes

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

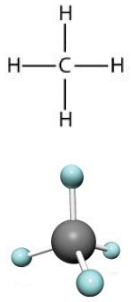


Figure **18.2.1**. Two dimensional model of methane (top); *Three-dimensional representation of methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron. (bottom)*

The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule.

condensed structural formula

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

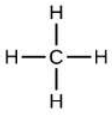
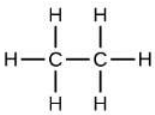
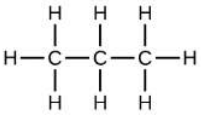
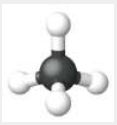
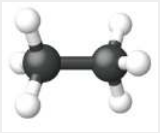
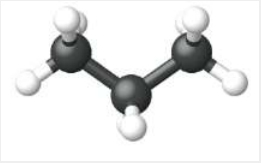


The ultimate condensed formula is a **line-angle formula (or line drawing)** , in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Pentane Isopentane

Table **18.2.1** Structural formulas for methane, ethane , and propane

Structural Formula			
Ball and Stick Model			
Space Filling model			
Name	Methane	Ethane	Propane
Condensed Structural Formula	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
Molecular Formula	CH_4	C_2H_6	C_3H_8
Line angle drawing			

Example 18.2.1

Provide the molecular formula, the complete structural formula, the condensed structural formula and the line angle formula for a straight chain alkane with 8 carbon atoms.

Solutions

Example **18.2.2** writing formulas for a straight chain alkane with eight carbon atoms.

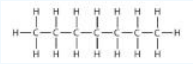
structural formula	Explanation	Answer
ula Molecular Formula	The general formula for an alkane is C_nH_{2n+2} For an alkane with 8 carbon atoms, $C_8H_{(2\times 8)+2} = C_8H_{18}$.	C_8H_{18}.
ula Complete Structural Formula	Eight carbons first linked together and all remaining bonds to hydrogen to fulfill the octet rule.	C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8
ula Condensed Structural Formula	The terminal carbon atoms (C_1 and C_8) are bonded to three hydrogen atoms each and the six middle carbon atoms are bonded to two hydrogen atoms each. The six middle carbon atoms are all bonded to two hydrogen atoms so the structural formula can be simplified further.	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ $CH_3(CH_2)_6CH_3$
ula Line Angle Drawing	Eight carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.	

? Exercise 18.2.1

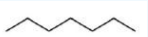
Provide the molecular formula, the complete structural formula, the condensed structural formula, and the line angle formula for a straight chain alkane with 7 carbon atoms.

Answer

molecular formula: C_7H_{16}

complete structural formula: 

condensed structural formula: $CH_3(CH_2)_5CH_3$

line angle drawing: 

Homologous Series

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table **18.2.1**.

Table **18.2.1** The First 10 Straight-Chain Alkanes

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

Note

Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Consider the series in Figure **18.2.2**. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

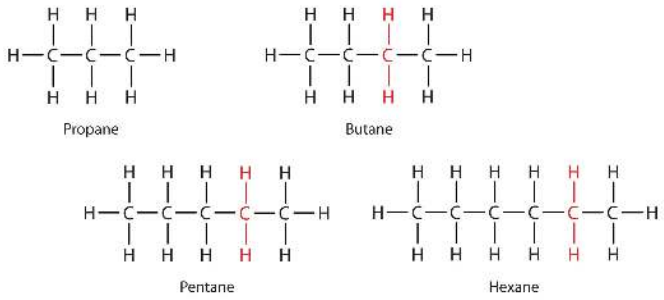


Figure **18.2.2** Members of a homologous series.

The principle of homology allows us to write a general formula for alkanes: $C_nH_{2n\,+\,2}$. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\,\times\,8)\,+\,2} = C_8H_{18}$.

Naming (IUPAC Nomenclature)

A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. A stem name in Table **18.2.1** indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers.

Table **18.2.2***Stems That Indicate the Number of Carbon Atoms in Organic Molecules*

Stem	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Note

A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

Example 18.2.2

What is the name of an eight carbon alkane?

Solution

The stem that refers to eight carbon atoms is **oct** plus the suffix **-ane** for an alkane, so the answer is **Octane**.

Exercise 18.2.2

Provide the name for the following compounds:

a. seven carbon alkane

b. six carbon alkane

Answer

a. heptane

b. hexane

Isomerism-Branched Chain Alkanes

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged - the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkanes and alkenes.

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

–C–C–C–C–

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

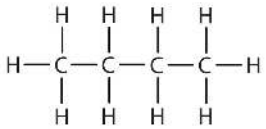


Figure **18.2.2** Complete structural formula of butane

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

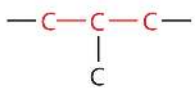
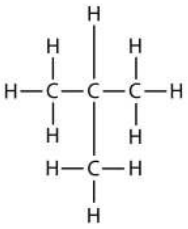


Figure **18.2.3** Incomplete structural formula

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



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

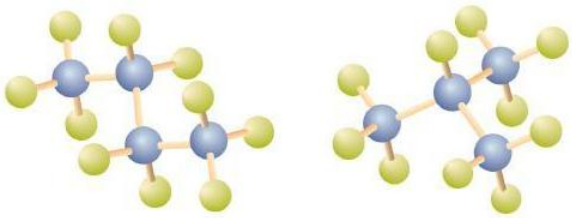
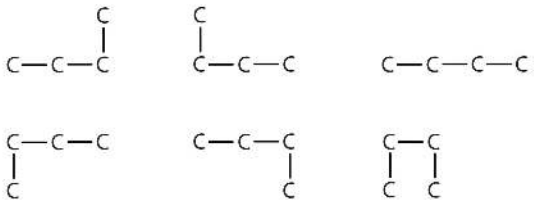


Figure **18.2.4** Butane and isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C4H10.

Notice that C_4H_{10} is depicted with a bent chain in Figure **18.2.4**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **18.2.4**.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.

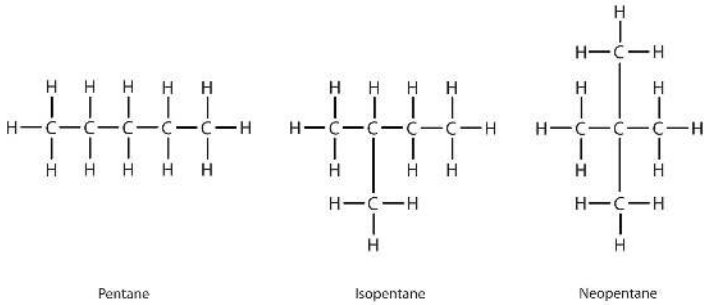


Figure **18.2.5** complete structural formulas for pentane isopentane and neopentane

Naming Branched Alkanes

You have already learned the basics of nomenclature-the names of the first 10 normal hydrocarbons. Here, we will add some steps to the procedure so you can name branched hydrocarbons.

First, given the structure of an alkane, identify the longest continuous chain of C atoms. Note that the longest chain may not be drawn in a straight line. The longest chain determines the parent name of the hydrocarbon. For example, in the molecule

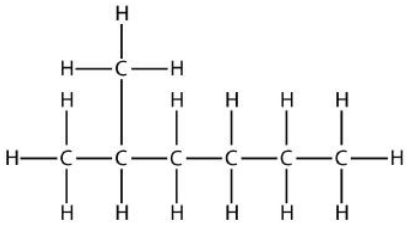


Figure **18.2.6** structural formula for hexane

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

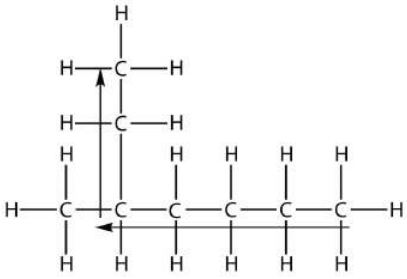


Figure **18.2.7** structural formula for heptane

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

The next step is to identify the branches, or **substituents,** on the main chain. The names of the substituents, or *alkyl groups*, are derived from the names of the parent hydrocarbons; however, rather than having the ending *-ane*, the substituent name has the ending *-yl*. Table **18.2.3**, lists the substituent names for the five smallest substituents.

***Table* 18.2.3** *Substituent Names.*

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

In naming the branched hydrocarbon, the name of the substituent is combined with the parent name of the hydrocarbon without spaces. However, there is likely one more step. The longest chain of the hydrocarbon must be numbered, and the numerical position of the substituent must be included to account for possible isomers. As with double and triple bonds, the main chain is numbered to give the substituent the lowest possible number. For example, in this alkane

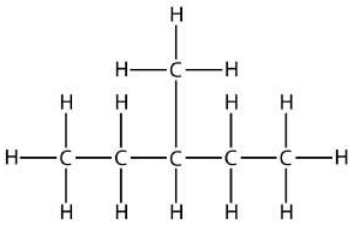


Figure **18.2.7** Structural formula for 3-methylpentane

the longest chain is five C atoms long, so it is a pentane. There is a one-carbon substituent on the third C atom, so there is a methyl group at position 3. We indicate the position using the number, which is followed by a hyphen, the substituent name, and the parent hydrocarbon name-in this case, **3-methylpentane**. That name is specific to that particular hydrocarbon and no other molecule. Organic chemistry nomenclature is very specific!

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

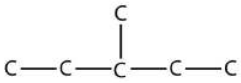
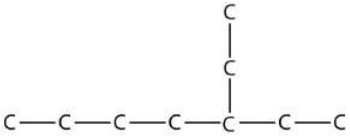


Figure **18.2.8** Structural formula for 3-methylpentane without the hydrogen atoms

where it is understood that any unwritten covalent bonds are bonds with H atoms. With this understanding, we recognize that the structural formula for 3-methylpentane refers to a molecule with the formula of C_6H_{14}.

Example 18.2.3:

Name this molecule.

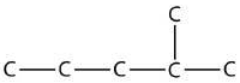


Solution

The longest continuous carbon chain has **seven** C atoms, so this molecule will be named as a **heptane**. There is a **two-carbon substituent** on the main chain, which is an **ethyl group**. To give the substituent the lowest numbering, we number the chain from the *right* side and see that **the substituent is on the third C atom**. So this hydrocarbon is **3-ethylheptane**.

Exercise 18.2.3

Name this molecule.



Answer

2-methylpentane

Branched hydrocarbons may have more than one substituent. If the substituents are different, then give each substituent a number (using the smallest possible numbers) and list the substituents in alphabetical order, with the numbers separated by hyphens and with no spaces in the name. So the molecule

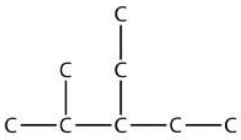


Figure **18.2.8** 3-ethyl-2-methylpentane

is 3-ethyl-2-methylpentane.

If the substituents are the same, then use the name of the substituent only once, but use more than one number, separated by a comma. Also, put a numerical prefix before the substituent name that indicates the number of substituents of that type. The numerical prefixes are listed in Table **18.2.4**. The number of the position values must agree with the numerical prefix before the substituent.

Table **18.2.4** Numerical Prefixes to Use for Multiple Substituents

Number of Same Substituent	Numerical Prefix
2	*di-*
3	*tri-*
4	*tetra-*
5	*penta-*
and so forth	and so forth

Consider this molecule:

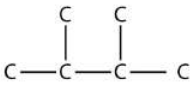
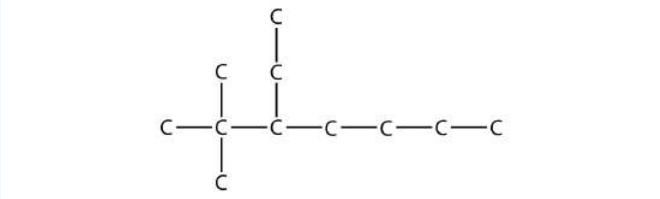


Figure **18.2.9** 2,3-dimethylbutane

The longest chain has four C atoms, so it is a butane. There are two substituents, each of which consists of a single C atom; they are methyl groups. The methyl groups are on the second and third C atoms in the chain (no matter which end the numbering starts from), so we would name this molecule 2,3-dimethylbutane. Note the comma between the numbers, the hyphen between the numbers and the substituent name, and the presence of the prefix *di-* before the *methyl*. Other molecules-even with larger numbers of substituents-can be named similarly.

Example 18.2.4:

Name this molecule.

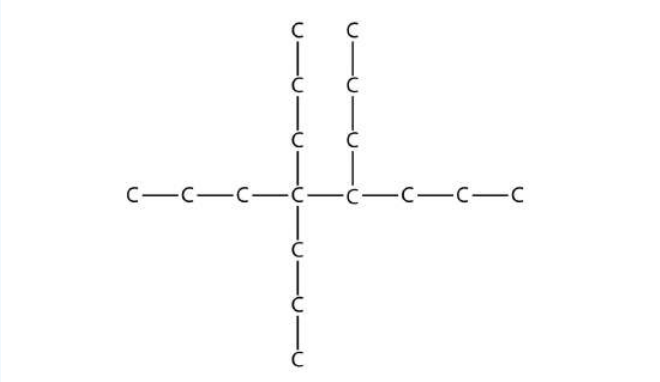


Solution

The longest chain has **seven** C atoms, so we name this molecule as a **heptane**. We find two one-carbon substituents on the second C atom and a **two-carbon substituent** on the third C atom. So this molecule is named **3-ethyl-2,2-dimethylheptane**.

Exercise 18.2.4

Name this molecule.



Answer

4,4,5-tripropyloctane

Properties of Alkanes

All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2}. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table **18.2.5**) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table **18.2.5** Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	Number of Structural Isomers
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

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

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure **18.2.10**). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

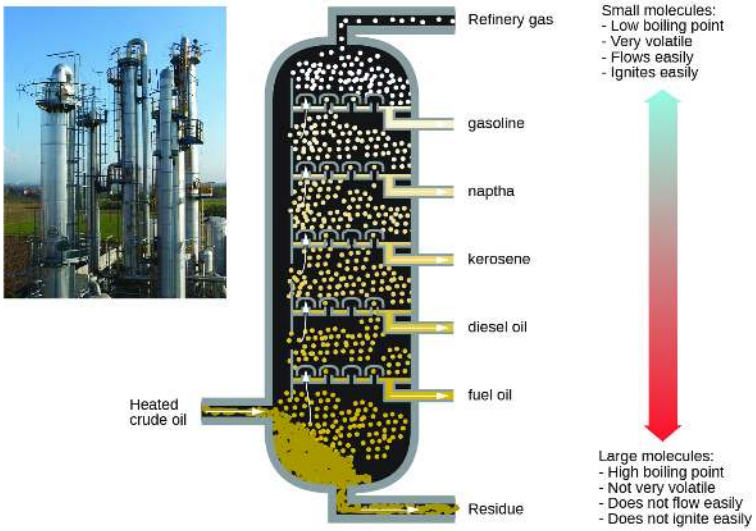


Figure 18.2.10 In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a substitution reaction, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:

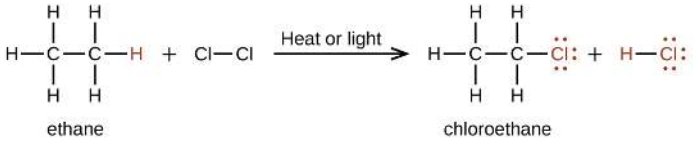


Figure 18.2.11 the reaction between ethane and molecular chlorine

The C–Cl portion of the chloroethane molecule is an example of a functional group, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

Cyclic Hydrocarbons

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds. Like other alkanes, cycloalkanes are saturated compounds. Cycloalkanes have the general formula C_nH_{2n}. The simplest cycloalkane shown below is cyclopropane, a three-carbon ring.

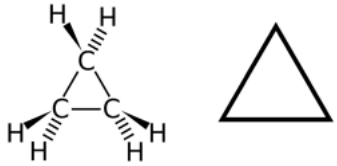


Figure 18.2.11 Cyclopropane the simplest cycloalkane.

The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left from the figure above. A convenient shorthand is to omit the element symbols and only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes are still sp^3 hybridized, with an ideal bond angle of 109.5°. However, an examination of the cyclopropane structure shows that the triangular structure results in a C–C–C bond angle of 60°. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane,

with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108°. This minimal ring strain for cyclopentane makes it a more stable compound.

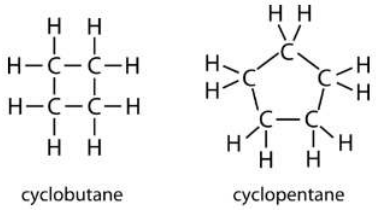


Figure 18.2.12 Cyclobutane and Cyclopentane

Cyclohexane is a six-carbon cycloalkane shown below

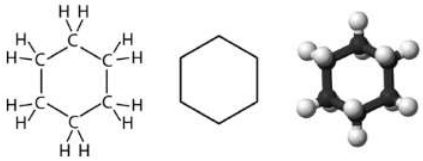


Figure 18.2.13 Cyclohexane

All three of the depictions of cyclohexane are somewhat misleading because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5°, the molecule is puckered. The puckering of the ring means that every other carbon atom is above and below the plane. The figure below shows two possibilities for the puckered cyclohexane molecule. Each of the structures is called a conformation. The conformation on the right is called the boat conformation, while the one on the left is called the chair conformation.

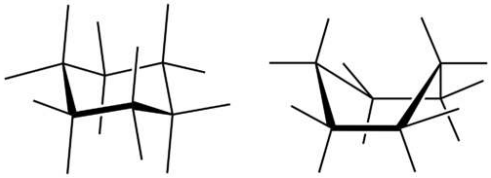


Figure 18.2.14 Chair (left) and boat (right) conformations for cyclohexane.

While both conformations reduce the ring strain compared to a planar molecule, the chair is preferred. This is because the chair conformation results in fewer repulsive interactions between the hydrogen atoms. However, interconversion readily occurs between the two conformations.

Larger cycloalkanes also exist, but are less common. Cyclic hydrocarbons may also be unsaturated. A **cycloalkene** is a cyclic hydrocarbon with at least one carbon-carbon double bond. A **cycloalkyne** is a cyclic hydrocarbon with at least one carbon-carbon triple bond. Shown below are the simplified structural formulas for cyclohexene and cyclooctyne.

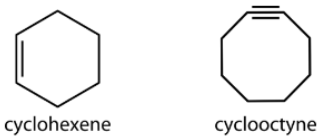


Figure 18.2.15 Cyclohexene(left) and cyclooctyne(right)

Unsaturated Hydrocarbons: Alkenes and Alkynes

Alkenes

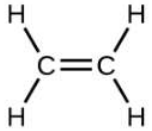
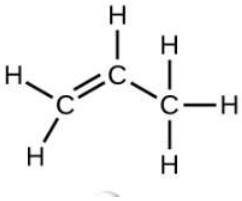
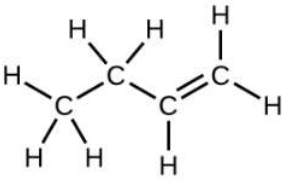
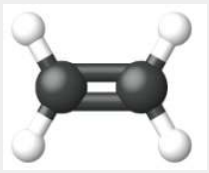
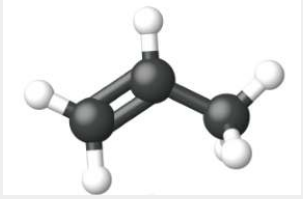
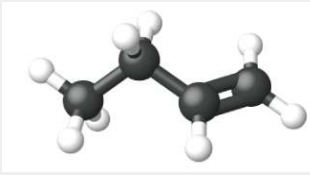
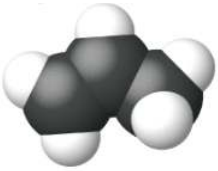
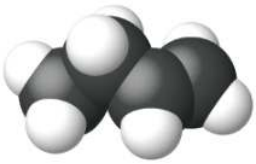
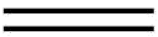
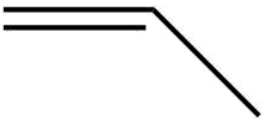
Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. Unsaturated hydrocarbons have less than the maximum number of H atoms possible. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Note

The word un*saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has at least one carbon-to-carbon double (C=C) or triple bond (C≡C).

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure **18.2.16**); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

Structural formulas of Alkenes

Structural Formula			
Ball and Stick Model			
Space Filling model			
Name	ethene	propene	1-butene
Condensed Structural Formula	CH_2CH_2	CH_2CHCH_3	$CH_3CH_2CHCH_2$
Molecular Formula	C_2H_2	C_3H_6	C_4H_8
Line angle drawing			

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:

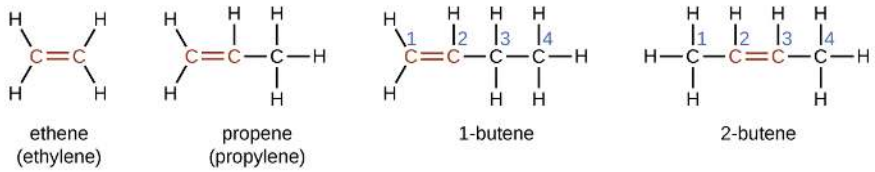


Figure **18.2.16** Four structural formulas and names are shown. The first shows two red C atoms connected by a red double bond illustrated with two parallel line segments. H atoms are bonded above and below to the left of the left-most C atom. Two more H atoms are similarly bonded to the right of the C atom on the right. Beneath this structure the name ethene and alternate name ethylene are shown. The second shows three C atoms bonded together with a red double bond between the red first and second C atoms moving left to right across the three-carbon chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the middle C atom. Three more H atoms are bonded above, below, and to the right of the third C atom. Beneath this structure the name propene and alternate name propylene is shown. The third shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red first and second carbon in the chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the second C atom. H atoms are bonded above and below the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 1 dash butene is shown. The fourth shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red second and third C atoms in the chain. H atoms are bonded above, below, and to the left of the left-most C atom. A single H atom is bonded above the second C atom. A single H atom is bonded above the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 2 dash butene is shown.

Alkynes

Hydrocarbon molecules with one or more triple bonds are called alkynes; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:



ethyne (acetylene)

Figure **18.2.17** The structural formula and name for ethyne, also known as acetylene, are shown. In red, two C atoms are shown with a triple bond illustrated by three horizontal line segments between them. Shown in black at each end of the structure, a single H atom is bonded.

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $\mathbf{CH_3CH_2C \equiv CH}$ is called 1-butyne.

Naming Alkenes and Alkynes

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

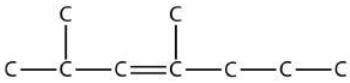
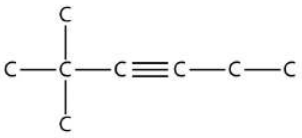


Figure **18.2.18** 2,4-dimethyl-3-heptene

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

Example 18.2.5

Name this molecule.

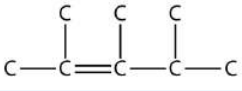


Solution

The longest chain that contains the C–C triple bond has six C atoms, so this is a hexyne molecule. The triple bond starts at the third C atom, so this is a 3-hexyne. Finally, there are two methyl groups on the chain; to give them the lowest possible number, we number the chain from the left side, giving the methyl groups the second position. So the name of this molecule is 2,2-dimethyl-3-hexyne.

? Exercise 18.2.5

Name this molecule.

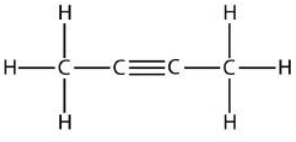
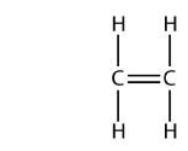
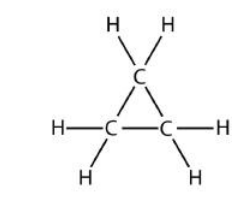


Answer

2,3,4-trimethyl-2-pentene

✓ Example 18.2.6

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

1. 
2. 
3. 

Solution

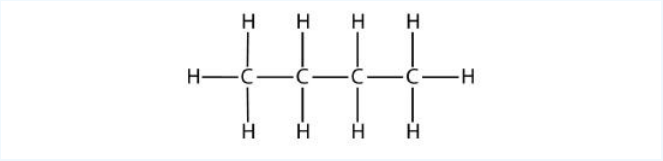
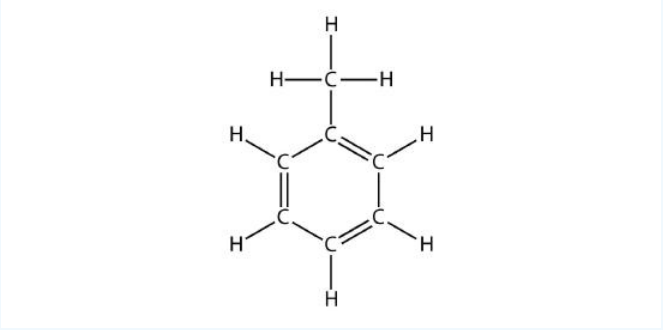
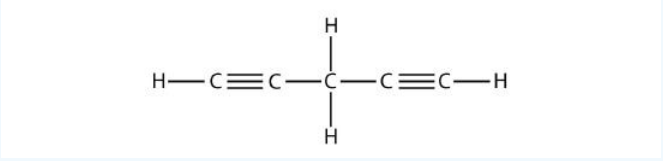
1. The molecule has at least one carbon-to-carbon triple bond (C≡C) so it is an **alkyne**.

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

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

? Exercise 18.2.6

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

1. 
2. 
3. 

Answer

1. alkane, 2. alkene, 3. alkyne

Properties of Alkenes and Alkynes

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen reacts with the C–C double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is

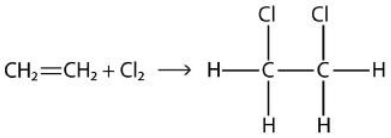


Figure 18.2.19

$$CH_2=CH_2 + H_2 \xrightarrow{metal\ catalyst} CH_3CH_3$$

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

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

$$CH_2=CH_2 + H_2 \xrightarrow{metal\ catalyst} CH_3CH_3$$

Geometric Isomers (Cis-Trans) Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.

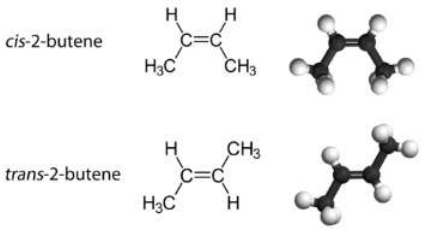


Figure **18.2.20**\ *cis*-2-butene and *trans*-2-butene.

The ***cis* isomer** has the two single hydrogen atoms on the same side of the molecule, while the ***trans* isomer** has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.

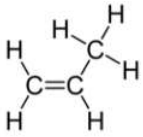


Figure **18.2.21**\ Propene

Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point,the now single bond is free to rotate and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.
- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.
- Alkanes have both common names and systematic names, specified by IUPAC.
- Names and structures of typical cyclic hydrocarbons are given.
- Structural and geometric isomers are defined.
- Examples of alkane and alkene isomers are given.

Contributors and Attributions

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- TextMap: Beginning Chemistry (Ball et al.)
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18.3: Aromatic Compounds- Benzene and Its Relatives

Learning Objective

- Name and identify aromatic compounds.

Benzene is the parent compound of the large family of organic compounds known as aromatic compounds. Unlike cyclohexane, benzene only contains six hydrogen atoms, giving the impression that the ring is unsaturated and each carbon atom participates in one double bond. Two different structures with alternating single and double bonds around the ring can be written for benzene.

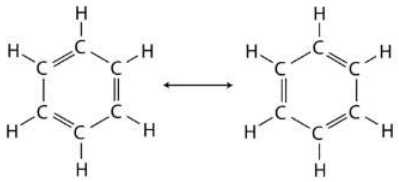


Figure **18.3.1** benzene

In benzene, the true bonding between carbon atoms is neither a single nor a double bond. Rather, all of the bonds are a hybrid of a single and double bond. In benzene, the pi bonding electrons are free to move completely around the ring. **Delocalized electrons** are electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more. The delocalization of the electrons in benzene can best be shown by showing benzene with a ring inside the hexagon, with the hydrogen atoms understood.



Figure **18.3.2** Delocalized electrons

Delocalization of the electrons makes for a more stable molecule than a similar molecule that does not have delocalized electrons. Benzene is a more stable and less reactive compound than straight-chain hexenes. The sp^2 hybridization of the carbon atoms results in a planar molecule as opposed to the puckered structure of cyclohexane.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:

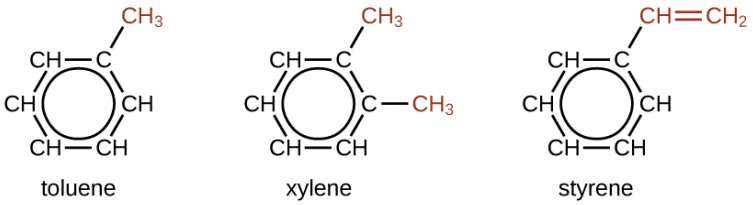


Figure **18.3.3** Three structural formulas are shown. The first is labeled toluene. This molecule has a six carbon hydrocarbon ring in which five of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a red C H subscript 3 group attached. A circle is at the center of the ring. The second is labeled xylene. This molecule has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have C H subscript 3 groups attached. These C H subscript 3 groups appear in red. A circle is at the center of the ring. The third is labeled styrene. This molecule has a six carbon hydrocarbon ring in which five of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a red C H double bond C H subscript 2 group attached. A circle is at the center of the ring.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene. The figure below shows the structural formulas for vanilla and naphthalene. Naphthalene is a chemical which is commonly used in mothballs. The vanilla molecule is extracted from vanilla beans.

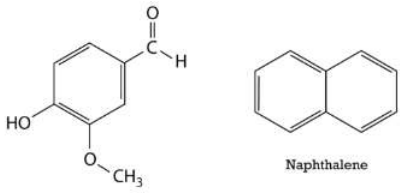


Figure 18.3.4 (left) vanilla molecule ; (right) naphthalene

Nomenclature of Aromatic Compounds

The simplest aromatic compounds are benzene rings with one substituent replacing one of the hydrogen atoms. If this substituent is an alkyl group, it is named first, followed in one word with "benzene". The molecule shown below is therefore called ethylbenzene.

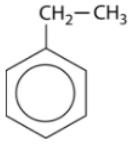


Figure 18.3.5 ethylbenzene

Substituents can be groups other than alkyl groups. If a chlorine atom were substituted for a hydrogen, the name becomes chlorobenzene. An $-NH_2$ group is called an amino group, so the corresponding molecule is called aminobenzene, often referred to as an aniline. An $-NO_2$ group is called a nitro group and so the third example below is nitrobenzene.

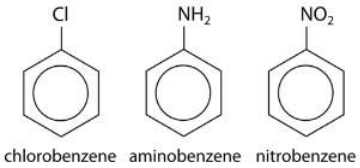


Figure 18.3.6 from left to right: chlorobenzene; aminobenzene; nitrobenzene

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

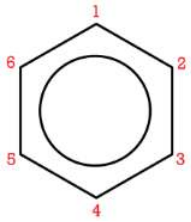


Figure 18.3.7 substituent locations relative to each other can be indicated by numbering the positions on the benzene ring

The number of the carbon location then precedes the name of the substituent in the overall name, with the numbers separated by a comma. As with branched alkanes, the system requires that the numbers be the lowest possible and that prefixes be used for more than one of the same substituent. If there are different substituents, the first in alphabetical order is given the lower number and listed first. The structures below are called 1,2-dimethylbenzene and 1-ethyl-4-methylbenzene.

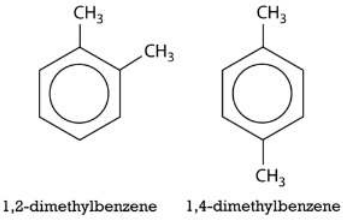


Figure 18.3.8 1,2-dimethylbenzene (left); 1-ethyl-4-methylbenzene (right)

An alternate system for naming di-substituted benzene rings uses three different prefixes: *ortho*, *meta*, and *para*. If two groups are in the **ortho** position, they are on adjacent carbon atoms. The **meta** positioning refers to being in a 1,3 arrangement. The **para** positioning refers to being in a 1,4 arrangement. Shown below are the three possibilities for dimethylbenzene, also called xylene.

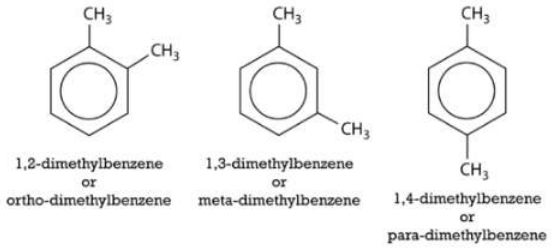


Figure **18.3.9** from left to right: ortho-dimethylbenzene; meta-dimethylbenzene ; para-dimethylbenzene

Lastly, a benzene ring missing one hydrogen atom ($-C_6H_5$) can itself be considered the substituent on a longer chain of carbon atoms. That group is called a *phenyl* group and so the molecule below is called 2-phenylbutane.

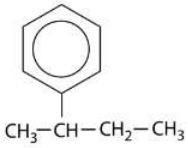


Figure **18.3.10** 2-phenylbutane

Summary

- Aromatic hydrocarbons contain ring structures with delocalized π electron systems.
- Benzene is the parent compound of the large family of organic compounds known as aromatic compounds.
- Naming of aromatic compound i.e. benzene rings with different substituents is described.

Contributors and Attributions

-
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18.4: Halogenated Hydrocarbons- Many Uses, Some Hazards

Learning Objectives

- Identify haloalkanes (alkyl halides) and know their occurrence, uses, and properties.
- Learn how to name simple haloalkanes.

Haloalkanes also known as alkyl halides or halogenoalkanes, are a group of organic compounds in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon. Haloalkanes are widely used commercially and, consequently, are known under many chemical and commercial names. Although these compounds were once widely used as dry cleaning solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants, increasing awareness of their toxicity and impact on the environment has led to a widespread decrease in applications for these materials.

The general formulas for organic molecules with functional groups use the letter **R** to stand for the rest of the molecule outside of the functional group. Because there are four possible halogen atoms (fluorine, chlorine, bromine, or iodine) that can act as the functional group, we use the general formula **R–X** to represent an alkyl halide.

Haloalkanes have higher boiling points than alkanes containing the same number of carbons. They are at best only slightly soluble in water but tend to dissolve in organic solvents.

Chloromethane (or methylchloride, CH_3Cl) was a widely used refrigerant, but its use has been discontinued due to its toxicity and flammability. Methyl chloride was also once used for producing lead-based gasoline additives (tetramethyllead).

The most important use of chloromethane today is as a chemical intermediate in the production of silicone polymers. Smaller quantities are used as a solvent in the manufacture of butyl rubber and in petroleum refining.

Large amounts of methyl chloride are produced naturally in the oceans by the action of sunlight on biomass and chlorine in sea foam. However, all methyl chloride that is used in industry is produced synthetically. Most methyl chloride is prepared by reacting methanol with hydrogen chloride, according to the chemical equation

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

This can be carried out either by bubbling hydrogen chloride gas through boiling methanol with or without a zinc chloride catalyst, or by passing combined methanol and hydrogen chloride vapors over an alumina catalyst at 350 °C (662 °F).

A smaller amount of chloromethane is produced by heating a mixture of methane and chlorine to over 400 °C (752 °F). However, this method also results in more highly chlorinated compounds such as dichloromethane, chloroform, and carbon tetrachloride and is usually only used when these other products are also desired.

Short chain haloalkanes such as dichloromethane (CH_2Cl_2), trichloromethane (chloroform, $CHCl_3$) and tetrachloromethane (carbon tetrachloride, CCl4) are commonly used as hydrophobic solvents in chemistry. They were formerly very common in industry; however, their use has been greatly curtailed due to their toxicity and harmful environmental effects.

Some specific compounds are still used. Halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) is still used in some situations as an inhalation anesthetic. The compound DDT is a very effective pesticide, but is only used when nothing else works because of its harmful effects on the environment.

Naming Alkyl Halides

IUPAC System: The rules for naming simple alkyl halides are listed below.

1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the halogen. Add a prefix for the particular halogen atom. The prefixes for each of the four halogens are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. If more than one kind of halogen atom is present, put them in alphabetical order. If there is more than one of the same halogen on a given carbon atom, use the prefixes *di-*, *tri-*, or *tetra-* before the prefix for the halogen.
2. As with hydrocarbons, number the carbon chain in a way that makes the sum of halogen numbers as low as possible. If different halogens are in equivalent positions, give the lower number to the one that comes first in alphabetical order.

3. Add the numerical prefix into the name before the halogen prefix.
4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Listed below are some examples of names and structural formulas of a few alkyl halides.

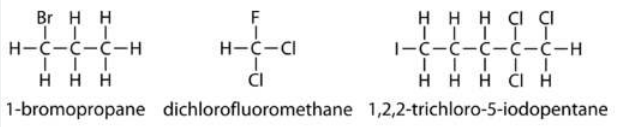


Figure **18.4.1** from left to right: 1-bromopropane; dichlorofluoromethane; 1,2,2-trichloro-5-iodpentane

Note that for the structure based on methane, no number needs to be used since there is only one carbon atom. In the third example, the *chloro-* is listed first alphabetically and the chain is numbered so that the sum of the numbers is as low as possible.

Common Names: The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*.

Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 18.4.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2$–) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

Exercise 18.4.1

Give common and IUPAC names for each compound.

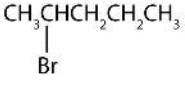
a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

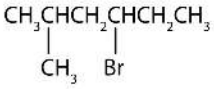
Answers

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

Example 18.4.2

Give the IUPAC name for each compound.

1. 

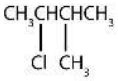


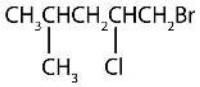
Solution

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl ($CH_{3)}$ and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

? Exercise 18.4.2

Give the IUPAC name for each compound.

a. 

- 

Answers

a. 2-chloro-3-methylbutane
b. 1-bromo-2-chloro-4-methylpentane

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table **18.4.1**, along with some of their uses.

Table **18.4.1**: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

Chlorofluorocarbons and Fluorocarbons

Chlorofluorocarbons (**CFCs**) and **hydrochlorofluorocarbons** (**HCFCs**) are fully or partly halogenated paraffin hydrocarbons that contain only carbon (C), hydrogen (H), chlorine (Cl), and fluorine (F), produced as volatile derivative of methane, ethane, and propane. They are also commonly known by the DuPont brand name **Freon**. The most common representative is dichlorodifluoromethane (R-12 or Freon-12). Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents. Because CFCs contribute to ozone depletion in the upper atmosphere, the manufacture of such compounds has been phased out under the Montreal Protocol, and they are being replaced with other products such as **hydrofluorocarbons** (HFCs)

Chlorinated or fluorinated alkenes undergo polymerization. Important halogenated polymers include polyvinyl chloride (PVC), and polytetrafluoroethene (PTFE, or Teflon). Billions of kilograms of chlorodifluoromethane are produced annually as precursor to tetrafluoroethylene, the monomer that is converted into Teflon. The production of these materials releases substantial amounts of wastes. PVC and PTFE will be discussed in more detail in Chapter 10.

Summary

- **Haloalkanes** also known as alkyl halides or halogenoalkanes, are a group of organic compounds in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon.
- These compounds are used as dry cleaning, industrial, and laboratory solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants
- The use of haloalkanes has been greatly curtailed due to their toxicity and harmful environmental effects.
- Naming of simple haloalkanes is described.

Contributors and Attributions

-
- Marisa Alviar-Agnew (Sacramento City College)
- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Wikipedia

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18.5: The Functional Group

Learning Objectives

- Define *functional group*.
- Identify the functional group(s) present in organic compounds.

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation **R** is used in some examples. The letter **R** is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see **R, R', or R"** which indicates that the R groups in the molecule can be different from one another. For example, R might be $–CH_2CH_3$ while R' is $–CH_2CH_2CH_2CH_3$.

The structure of capsaicin, the compound responsible for the heat in peppers, incorporates several functional groups, labeled in the figure below and explained throughout this section.

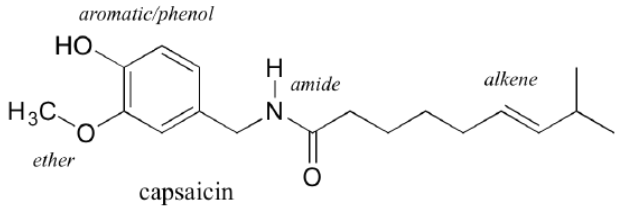


Figure 18.5.1 The structure of capsaicin

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

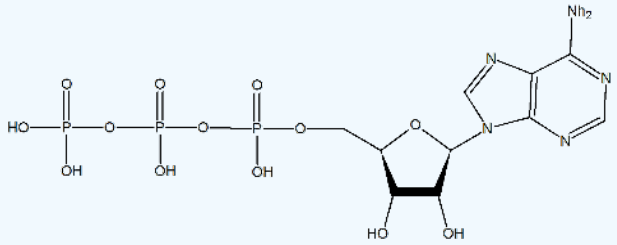
Table 18.5.1 Selected Organic Functional Groups

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	C═C	C_2H_4	ethene
alkyne	C≡C	C_2H_2	ethyne
alcohol	R—O—H	CH_3CH_2OH	ethanol
ether	R—O—R′	$(C_2H_5)_2O$	diethyl ether
aldehyde	R—C(=O)—H	CH_3CHO	ethanal
ketone	R—C(=O)—R′	$CH_3COCH_2CH_3$	methyl ethyl ketone
carboxylic acid	R—C(=O)—O—H	CH_3COOH	acetic acid
ester	R—C(=O)—O—R′	$CH_3CO_2CH_2CH_3$	ethyl acetate
amine	R—N(—H)(—H) R—N(—H)(—R′) R—N(—R′)(—R″)	$C_2H_5NH_2$	ethylamine
amide	R—C(=O)—N(—H)—R′	CH_3CONH_2	acetamide

Figure 18.5.1

Example 18.5.1

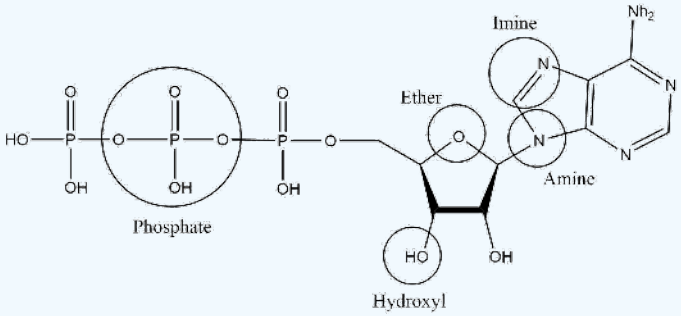
Identify the common functional groups for ATP.



Example 18.5.1

Solution

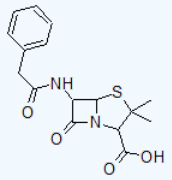
The common functional groups for ATP are **hydroxyl**, **ether** and **amine**. The other functional groups are covered in higher organic chemistry courses.



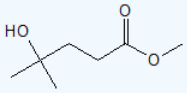
Example 18.5.1 ATP

Exercise 18.5.1

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



penicillin

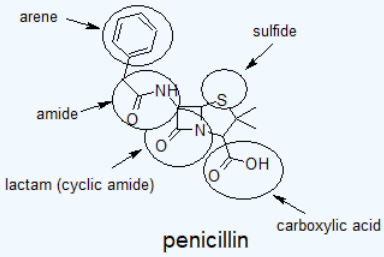




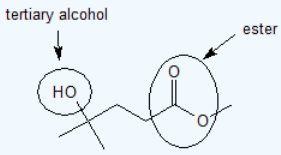
pyruvic acid

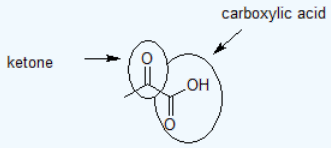


Answer

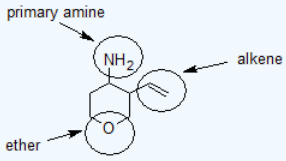


penicillin





pyruvic acid



Summary

- Functional groups consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). It can determine the chemical reactivity of a molecule under a given set of conditions
- The major families of organic compounds are characterized by their functional groups.

Contributors and Attributions

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18.6: Alcohols, Phenols, and Ethers

Learning Objectives

- Describe the structure and properties of alcohols, ethers and phenols.
- Know the name and uses of simple alcohols, phenols and ethers.

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:

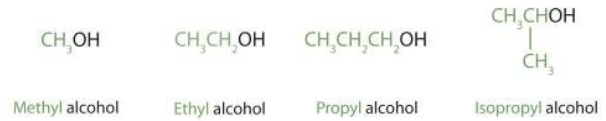
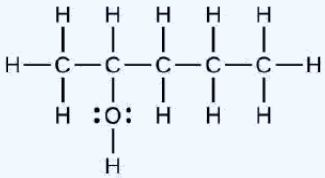


Figure **18.6.1**:left to right: methyl alcohol; ethyl alcohol; propyl alcohol; isopropyl alcohol

According to the International Union of Pure and Applied Chemistry (IUPAC), the name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.

Example 18.6.1: Naming Alcohols

Consider the following example. How should it be named?

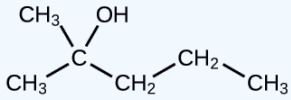


Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

Exercise 18.6.1

Name the following molecule:



Exercise **18.6.1**: The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

Answer

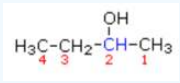
2-methyl-2-pentanol

Note

The IUPAC adopted new nomenclature guidelines in 2013 that require this number to be placed as an “infix” rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time, and students are encouraged to be familiar with both the old and new naming protocols.

Example 18.6.2: Naming Alcohols

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



Example **18.6.2**:

Solution

The carbon chain contains four carbon atoms. If the hydroxyl group was not present, we would have named this molecule butane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule butan-2-ol.

Note

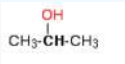
"Always place the OH on the lowest possible number for the chain."

In the previous example, if the carbon atoms were numbered from left to right then the OH would have been placed on the third carbon and the molecule would have been named butan-3-ol, but butan-2-ol is the more preferred name.

Exercise 18.6.2: Naming Alcohols

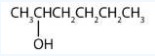
Name the following molecules according to the guidelines adopted in 2013?

a.



Exercise **18.6.2**:

b.



Exercise **18.6.2**:

Answer

a. propan-2-ol

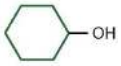
b. hexan-2-ol

Table **18.6.1** names and classifies some of the simpler alcohols. Some of the common names reflect a compound’s classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Figure **18.6.2**: from left to right: isobutyl alcohol press; sec-butyl alcohol;tert-butyl alcohol

Table **18.6.1**: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Common Name	IUPAC Name
CH_3OH	wood alcohol (methyl alcohol)	methanol
CH_3CH_2OH	grain alcohol (ethyl alcohol)	ethanol
$CH_3CH_2CH_2OH$	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	rubbing alcohol (isopropyl alcohol)	2-propanol
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	1-butanol
$CH_3CH_2CHOHCH_3$	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	*tert*-butyl alcohol	2-methyl-2-propanol
	cyclohexyl alcohol	cyclohexanol

Methanol (Methyl Alcohol)

Methanol, also known as **methyl alcohol** among others, is a chemical with the formula CH_3OH (a methyl group linked to a hydroxyl group, often abbreviated MeOH). Methanol acquired the name **wood alcohol** because it was once produced chiefly by the destructive distillation of wood. Today, methanol is mainly produced industrially by hydrogenation of carbon monoxide.

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$$

Methanol is the simplest alcohol, consisting of a methyl group linked to a hydroxyl group. It is a light, volatile, colorless, flammable liquid with a distinctive odor similar to that of ethanol (drinking alcohol). At room temperature, it is a polar liquid. With more than 20 million tons produced annually, it is used as a fuel additive and as a precursor to other commodity chemicals, including formaldehyde, acetic acid, methyl tert-butyl ether, as well as a host of more specialized chemicals.

Ethanol (Ethyl Alcohol)

Ethanol (also called **ethyl alcohol**, **grain alcohol**, **drinking alcohol**, or simply **alcohol**) is a chemical compound, a simple alcohol with the chemical formula C_2H_6O. Its formula can be also written as $CH_3{-}CH_2{-}OH$ or C_2H_5OH (an ethyl group linked to a hydroxyl group), and is often abbreviated as **EtOH**. Ethanol is a volatile, flammable, colorless liquid with a slight characteristic odor. It is a psychoactive substance and is the principal type of alcohol found in alcoholic drinks.

Ethanol is naturally produced by the fermentation of sugars by yeasts or via petrochemical processes, and is most commonly consumed as a popular recreational drug. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:

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

Figure **18.6.3**: Fermentation of glucose to ethanol

Large quantities of ethanol (for industrial use) are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:

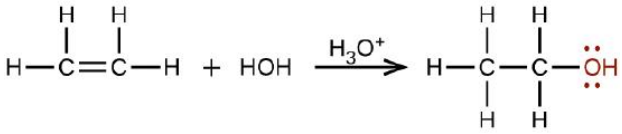


Figure 18.6.4 This reaction shows two carbons connected by a double bond, each with two bonded H atoms plus H O H arrow labeled “H subscript 3 O superscript plus” followed by two carbon atoms connected with a single bond with 5 bonded H atoms and an O H group shown in red at the right end of the molecule. The O of this group is shown with 2 pairs of electron dots.

Ethanol also has medical applications as an antiseptic and disinfectant. The compound is widely used as a chemical solvent, either for scientific chemical testing or in synthesis of other organic compounds, and is a vital substance used across many different kinds of manufacturing industries. Ethanol is also used as a clean-burning fuel source.

Toxicity of Alcohols

With respect to acute toxicity, simple alcohols have low acute toxicities. Doses of several milliliters are tolerated. For pentanols, hexanols, octanols and longer alcohols, LD50 (lethal dose, 50%) range from 2–5 g/kg (rats, oral). Methanol and ethanol are less acutely toxic. Methanol is however far more toxic than ethanol. All alcohols are mild skin irritants.

The metabolism of methanol (and ethylene glycol) is affected by the presence of ethanol, which has a higher affinity for liver alcohol dehydrogenase. In this way methanol will be excreted intact in urine.

The immediate effect of alcohol depends on the drinker's blood alcohol concentration (BAC). BAC can be different for each person depending on their age, sex, pre-existing health condition, even if they drink the same amount of alcohol.

Different BACs have different effects. Table 18.6.2 list the common effects of alcohol on the body depending on the BAC. However, tolerance varies considerably between individuals, as does individual response to a given dosage; the effects of alcohol differ widely between people. Hence in this context, BAC percentages are just estimates used for illustrative purposes.

Table 18.6.2 Blood Alcohol Levels and Effects Source: Wikipedia.

mg/dL	mM	Blood Alcohol Level % v/v	Effects
50	11	0.05%	Euphoria, talkativeness, relaxation
100	22	0.1%	Central nervous system depression, nausea, possible vomiting, impaired motor and sensory function, impaired cognition
>140	30	>0.14%	Decreased blood flow to brain
300	65	0.3%	Stupefaction, possible unconsciousness
400	87	0.4%	Possible death
500	109	>0.55%	Death

Rubbing alcohol refers to either isopropyl alcohol (propan-2-ol) or ethanol based liquids. Rubbing alcohol is undrinkable even if it is ethanol based, due to the bitterants added. Product labels for rubbing alcohol include a number of warnings about the chemical, including the flammability hazards and its intended use only as a topical antiseptic and not for internal wounds or consumption. It should be used in a well-ventilated area due to inhalation hazards. Poisoning can occur from ingestion, inhalation, absorption, or consumption of rubbing alcohol.

Multifunctional Alcohols

A **polyol** is an organic compound containing multiple hydroxyl groups. Examples of polyols discussed in this section include ethylene glycol, propylene glycol, and glycerol.

Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):

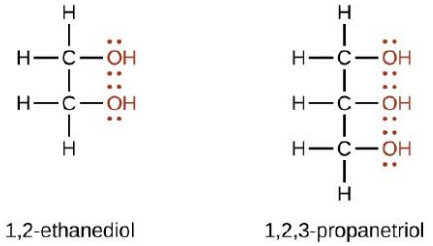


Figure **18.6.5**1,2-ethanediol; 1,2,3-propanetriol

Ethylene glycol (IUPAC name: ethane-1,2-diol) is an organic compound with the formula $(CH_2OH)_2$. It is mainly used for two purposes, as a raw material in the manufacture of polyester fibers and for antifreeze formulations. It is an odorless, colorless, sweet-tasting, viscous liquid. Ethylene glycol is toxic. Household pets are especially susceptible to ethylene glycol poisoning from vehicle antifreeze leaks.



Figure **18.6.6** from left to right:Ethylene glycol line model; Ethylene glycol ball and stick model*Fluorescent green-dyed antifreeze is visible in the radiator header tank when car radiator cap is removed.*



Propylene glycol (IUPAC name: **propane-1,2-diol**) is a organic compound with the chemical formula $CH_3CH(OH)CH_2OH$. It is a viscous, colorless liquid which is nearly odorless but possesses a faintly sweet taste. Containing two alcohol groups, it is classed as a diol. It is miscible with a broad range of solvents, including water, acetone, and chloroform. In general, glycols are non-irritating, have very low volatility and very low toxicity.

Figure **18.6.7** *A bottle of flavored "e-liquid" for "vaping" shows propylene glycol as the main ingredient. Source: Wikipedia*



Figure **18.6.8** **Propylene glycol**

Forty-five percent of propylene glycol produced is used as chemical feedstock for the production of unsaturated polyester resins. Propylene glycol is also used in various edible items such as coffee-based drinks, liquid sweeteners, ice cream, whipped dairy products and soda.Vaporizers used for delivery of pharmaceuticals or personal-care products often include propylene glycol among the ingredients. In alcohol-based hand sanitizers, it is used as a humectant to prevent the skin from drying. Propylene glycol is used as a solvent in many pharmaceuticals, including oral, injectable and topical formulations, such as for diazepam and lorazepam which are insoluble in water. Certain formulations of artificial tears, such as Systane, use proplyene glycol as an ingredient.Propylene glycol is frequently used as a substitute for ethylene glycol in low toxicity, environmentally friendly automotive antifreeze. It is also used to winterize the plumbing systems in vacant structures.

Glycerol (/ˈɡlɪsərɒl/; also called **glycerine** or **glycerin**; see spelling differences) is a simple polyol compound. It is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. The glycerol backbone is found in many lipids which are known as glycerides. It is widely used in the food industry as a sweetener and humectant in pharmaceutical formulations. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature.

Figure **18.6.9** Glycerol ball and stick model (top) line model (bottom)

In food and beverages, glycerol serves as a humectant, solvent, and sweetener, and may help preserve foods. It is also used as filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liqueurs. Glycerol and water are used to preserve certain types of plant leaves. As a sugar substitute, it has approximately 27 kilocalories per teaspoon (sugar has 20) and is

60% as sweet as sucrose. It does not feed the bacteria that form plaques and cause dental cavities.[*citation needed*] As a food additive, glycerol is labeled as E number E422. It is added to icing (frosting) to prevent it from setting too hard.

Glycerol is used in medical, pharmaceutical and personal care preparations, often as a means of improving smoothness, providing lubrication, and as a humectant. Ichthyosis and xerosis have been relieved by the topical use glycerin. It is found in allergen immunotherapies, cough syrups, elixirs and expectorants, toothpaste, mouthwashes, skin care products, shaving cream, hair care products, soaps, and water-based personal lubricants (Figure \(*PageIndex{10}*\)). In solid dosage forms like tablets, glycerol is used as a tablet holding agent.

Table \(\PageIndex{2}\) Blood Alcohol Levels and Effects Source: Wikipedia.

Figure **18.6.10** *Personal lubricants commonly contain glycerol.*

Phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

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

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive (“hospital smell”) odor.

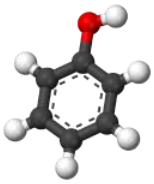


Figure **18.6.11** *Structure of phenol*



Figure **18.6.12**
Approximately two grams of phenol in glass vial. Image used with permisison from Wikipedia

To Your Health: Phenols and Us

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



Figure **18.6.13** *An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.*

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.

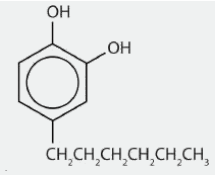


Figure **18.6.14** The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

In addition to acting as an antiseptic, phenol is also a useful precursor in many chemical syntheses to produce pharmaceuticals, food preservatives, polymers, resins and adhesives. Phenolics are also present in a number of biological systems and natural products such as neurotransmitters, flavouring agents, and vitamins to name a few.

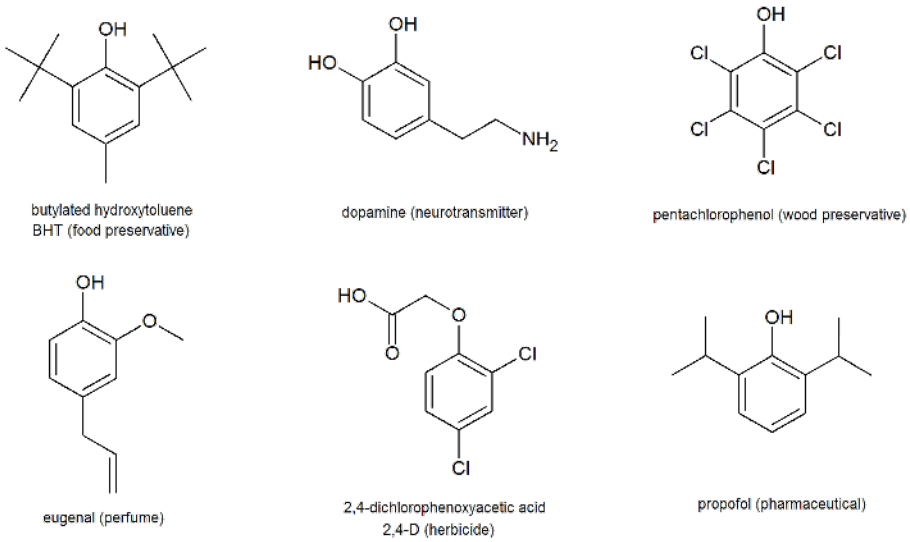


Figure **18.6.15** Top from left to right: line models of BHT; dopamine; pentachlorophenol; Bottom: eugenal; 2,4-dichlorophenoxyacetic acid; propofol

Ethers

Ethers are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named “methoxy.” The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers as shown below, are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by “ether.”

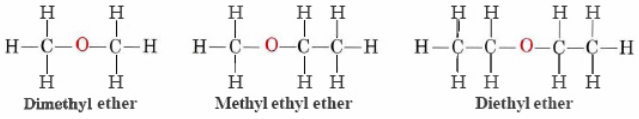


Figure **18.6.16** from left to right: Dimethyl ether; methyl ethyl ether; Diethyl ether

In the general formula for ethers, R—**O**—R, the hydrocarbon groups (R) may be the same or different.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table **18.6.3**).

Table **18.6.3** Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



Figure **18.6.17** *William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.*

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.

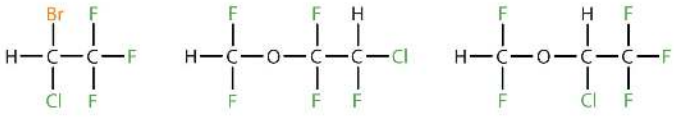
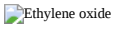


Figure 18.6.18 from left to right: halothane, enflurane, isoflurane. *These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.*

A list of important ethers and their uses are given in Table 18.6.4

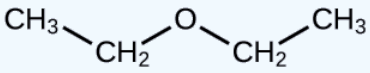
Table 18.6.4 Important Ethers and Their Uses

	Ethylene oxide	Also the simplest epoxide. Most ethylene oxide is used for synthesis of ethylene glycols (antifreeze), including diethylene glycol and triethylene glycol, that accounts for up to 75% of global consumption.
	Dimethyl ether	An aerosol spray propellant. A potential renewable alternative fuel for diesel engines with a cetane rating as high as 56–57.
	Diethyl ether	A common low boiling solvent (b.p. 34.6 °C) and an early anaesthetic. Used as starting fluid for diesel engines. Also used as a refrigerant and in the manufacture of smokeless gunpowder, along with use in perfumery.
	Dimethoxyethane(DME)	A water miscible solvent often found in lithium batteries (b.p. 85 °C):
	Dioxane	A cyclic ether and high-boiling solvent (b.p. 101.1 °C).

Example 18.6.2: classifying functional groups

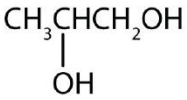
Identify the following compounds as alcohol, phenol or ether.

a.



Example 18.6.2:

b.



Example 18.6.2:

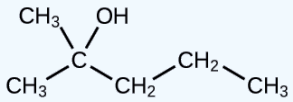
Solution

a. The compound has the general formula R—**O**—R, so it is an ether. b. The compound has two hydroxyl (–OH) groups, so it is an alcophol.

Exercise 18.6.2

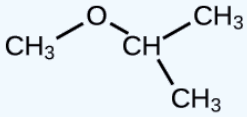
Identify the following compounds as alcohol, phenol or ether.

a.



Exercise **18.6.2**: The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

b.



Exercise **18.6.2**: A molecular structure shows a C H subscript 3 group bonded up and to the right to an O atom. The O atom is bonded down and to the right to a C H group. The C H group is bonded up and to the right to a C H subscript 3 group. The C H group is also bonded down and to the right to another C H subscript 3 group.

Answer

a. alcohol b. ether

Summary

- The –OH group is the functional group of an alcohol. Various alcohols have a wide range of applications in the medical field as well as in the transportation, food, cosmetic industries.
- The name of an alcohol comes from the hydrocarbon from which it was derived.
- The –R–O–R– group is the functional group of an ether. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. Ethylene oxide in particular is used in the manufacture of ethylene glycol (antifreeze).
- Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

Contributors and Attributions

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- TextMap: The Basics of GOB Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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18.7: Aldehydes and Ketones

Learning Objectives

- Describe the structure and properties of aldehydes and ketones.
- Name common aldehydes and ketones.

Aldehydes and ketones are widespread in nature and are often combined with other functional groups. Examples of naturally occurring molecules which contain a aldehyde or ketone functional group are shown in the following two figures. The compounds in Figure **18.7.1** are found chiefly in plants or microorganisms and those in Figure **18.7.2** have animal origins. Aldehydes and ketones are known for their sweet and sometimes pungent odors. The odor from vanilla extract comes from the molecule vanillin. Likewise, benzaldehyde provides a strong scent of almonds and is this author's favorite chemical smell. Because of their pleasant fragrances aldehyde and ketone containing molecules are often found in perfumes. However, not all of the fragrances are pleasing. In particular, 2-Heptanone provides part of the sharp scent from blue cheese and (R)-Muscone is part of the musky smell from the Himalayan musk deer. Lastly, ketones show up in many important hormones such as progesterone (a female sex hormone) and testosterone (a male sex hormone). Notice how subtle differences in structure can cause drastic changes in biological activity. The ketone functionality also shows up in the anti-inflammatory steroid, Cortisone.

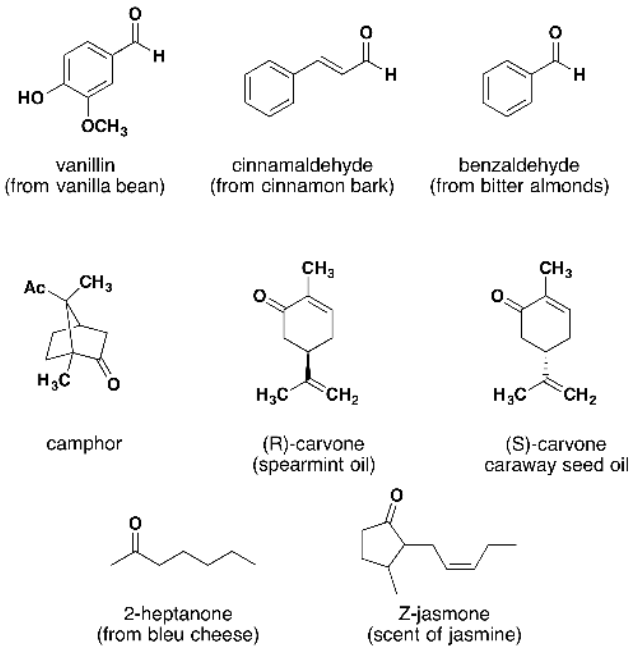


Figure **18.7.1** Aldehyde and ketone containing molecules isolated from plant sources.

Figure **18.7.1**

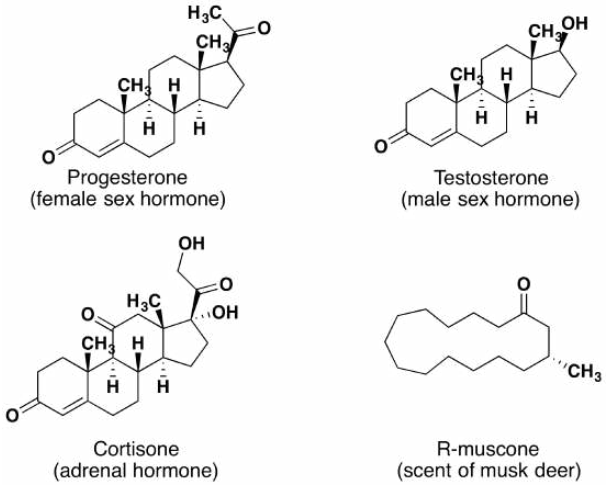


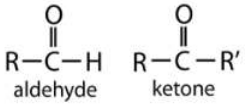
Figure **18.7.2** Aldehyde and ketone containing molecules isolated from animal sources.

Figure **18.7.1**

Aldehydes and **ketones** are two related categories of organic compounds that both contain the **carbonyl group**, shown below



The difference between aldehydes and ketones is the placement of the carbonyl group within the molecule. An **aldehyde** is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain. A **ketone** is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain. The general formulas for each are shown below.



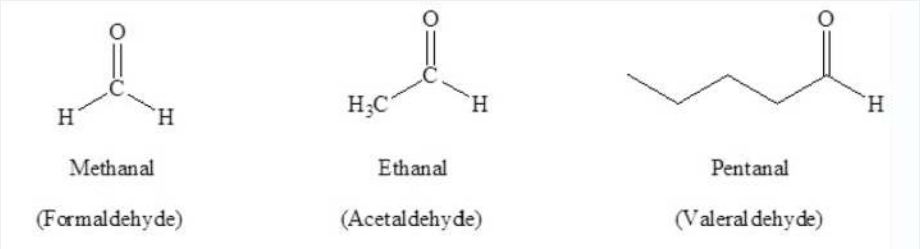
For aldehydes, the **R** group may be a hydrogen atom or any length carbon chain.

Naming Simple Aldehydes and Keones

Aldehydes are named by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-al*.

For the common name of aldehydes start with the common parent chain name and add the suffix ***-aldehyde***.

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



For ketones, **R** and **R′** must be carbon chains, of either the same or different lengths. The steps for naming ketones, followed by two examples, are shown below.

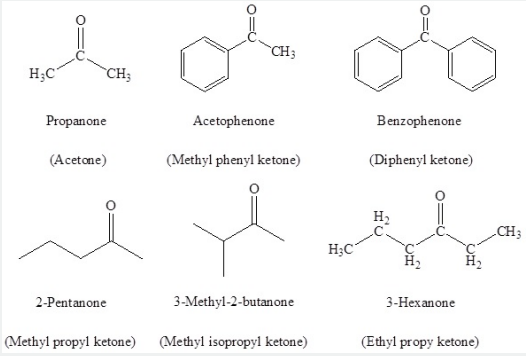
1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-one*.
2. Number the carbon atoms in the chain in a way that the carbonyl group has the lowest possible number.

3. Add the numerical prefix into the name before the name of the ketone.
4. Use a hyphen between the number and the name of the ketone.

The common name for ketones are simply the **substituent groups listed alphabetically + *ketone*.**

Some common ketones are known by their generic names. Such as the fact that *propanone* is commonly referred to as *acetone*.

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



Top from left to right:propanone (acetone); acetophenone (methyl phenol ketone); benzophenone (diphenyl ketone; Bottom from left to right: 2 pentanone (methyl propyl ketone); 3 methyl 2 butanone (methyl isopropyl ketone); 3 hexanone (ethyl propyl ketone)

Properties of Aldehydes and Ketones

Aldehydes and ketones can work weak hydrogen bonds with water through the carbonyl oxygen atom. The lower members of both series (3 carbons or fewer) are soluble in water in all proportions. As the length of the carbon chain increases, water solubility decreases. Similar to ethers, neither aldehydes nor ketones can hydrogen bond with themselves. As a result, their boiling points are generally lower than those of alcohols. Unlike alkanes however, aldehydes and ketones are polar molecules due to the more electronegative oxygen atom. The dipole-dipole interactions are stronger than the dispersion forces present in alkanes. The boiling points of aldehydes and ketones are intermediate between those of alkanes and alcohols. For example, the boiling point of ethane is $-89°C$, ethanal is $20°C$, and ethanol is $78°C$.

Methanal, commonly known as formaldehyde, was once commonly used as a biological preservative for dead animals. In recent years formaldehyde has been shown to be a carcinogen and so has been replaced for the purpose by safer alternatives. Aldehydes are currently used in the production of resins and plastics. The simplest ketone, propanone, is commonly called acetone. Acetone is a common organic solvent that was one used in most nail polish removers, but has largely been replaced by other solvents.

Some Common Aldehydes

Formaldehyde, an aldehyde with the formula HCHO, is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Formaldehyde is produced industrially by the catalytic oxidation of methanol according to the chemical equation:

$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O$$

Acetaldehyde (systematic name **ethanal**) is an organic chemical compound with the formula CH_3CHO, sometimes abbreviated by chemists as MeCHO (Me = methyl). It is one of the most important aldehydes, occurring widely in nature and being produced on a large scale in industry. Acetaldehyde occurs naturally in coffee, bread, and ripe fruit, and is produced by plants.

In 2003, global production was about 1 million tonnes. Before 1962, ethanol and acetylene were the major sources of acetaldehyde. Since then, ethylene is the dominant feedstock.

The main method of production is the oxidation of ethylene by the Wacker process, which involves oxidation of ethylene using a homogeneous palladium/copper system:

$$2\ CH_2{=}CH_2 + O_2 \rightarrow 2\ CH_3CHO$$

Propionaldehyde or **propanal** is the organic compound with the formula CH_3CH_2CHO. It is a saturated 3-carbon aldehyde and is a structural isomer of acetone. It is a colorless liquid with a slightly irritating, fruity odor. **Butyraldehyde**, also known as **butanal**, is an organic compound with the formula $CH_3(CH_2)_2CHO$. This compound is the aldehyde derivative of butane. It is a colourless flammable liquid with an unpleasant smell. It is miscible with most organic solvents. A major use of butyraldehyde is in the production of bis(2-ethylhexyl) phthalate, a major plasticizer. **Benzaldehyde** (C_6H_5CHO) is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde and one of the most industrially useful.It is a colorless liquid with a characteristic almond-like odor. The primary component of bitter almond oil, benzaldehyde can be extracted from a number of other natural sources. Synthetic benzaldehyde is the flavoring agent in imitation almond extract, which is used to flavor cakes and other baked goods

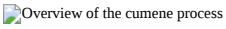
Traces of many aldehydes are found in essential oils and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin.

Some Common Ketones

In terms of scale, the most important ketones are acetone, methylethyl ketone, and cyclohexanone. They are also common in biochemistry, but less so than in organic chemistry in general.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. **Acetone** is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

Acetone is produced directly or indirectly from propylene. Approximately 83% of acetone is produced via the cumene process; as a result, acetone production is tied to phenol production. In the cumene process, benzene is alkylated with propylene to produce cumene, which is oxidized by air to produce phenol and acetone:



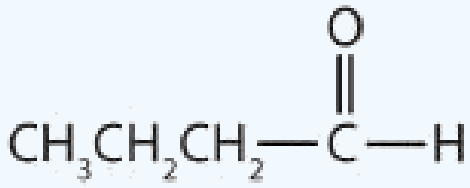
Other processes involve the direct oxidation of propylene (Wacker-Hoechst process), or the hydration of propylene to give 2-propanol, which is oxidized to acetone.

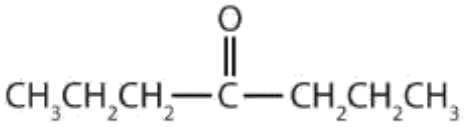
Butanone, also known as **methyl ethyl ketone** (**MEK**), is an organic compound with the formula $CH_3C(O)CH_2CH_3$. This colorless liquid ketone has a sharp, sweet odor reminiscent of butterscotch and acetone. It is produced industrially on a large scale, and also occurs in trace amounts in nature. It is soluble in water and is commonly used as an industrial solvent. Butanone is an effective and common solvent and is used in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films. For this reason it finds use in the manufacture of plastics, textiles, in the production of paraffin wax, and in household products such as lacquer, varnishes, paint remover, a denaturing agent for denatured alcohol, glues, and as a cleaning agent. It has similar solvent properties to acetone but boils at a higher temperature and has a significantly slower evaporation rate.

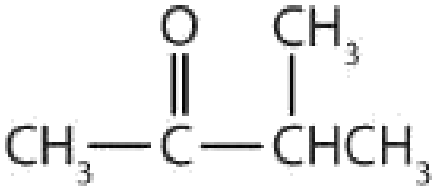
Cyclohexanone is the organic compound with the formula $(CH_2)_5CO$. The molecule consists of six-carbon cyclic molecule with a ketonefunctional group. This colorless oil has an odor reminiscent of that of acetone. Over time, samples of cyclohexanone assume a yellow color. Cyclohexanone is slightly soluble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

Example 18.7.1

Classify each compound as an aldehyde or a ketone.

a. 

b. 

c. 

Solution

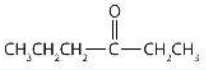
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

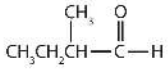
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone.

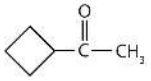
c. This compound has the carbonyl group between two alkyl groups, so it is a ketone.

? Exercise 18.7.1

Classify each compound as an aldehyde or a ketone.

a. 

b. 

c. 

Answer

a. ketone b. aldehyde c. ketone

Summary

- An aldehyde is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain.
- A ketone is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain.The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*.
- Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

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18.8: Carboxylic Acids and Esters

Learning Objectives

- Describe the structure and properties of carboxylic acids and esters.
- Name common carboxylic acids and esters.

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived.

Both carboxylic acids and esters contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):

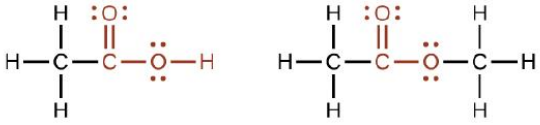


Figure 18.8.1 Two structures are shown. The first structure is labeled, “ethanoic acid,” and, “acetic acid.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. To the right of this in red is a bonded group comprised of a C atom to which an O atom is double bonded above. To the right of the red C atom, an O atom is bonded which has an H atom bonded to its right. Both O atoms have two sets of electron dots. The second structure is labeled, “methyl ethanoate,” and, “methyl acetate.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. In red, bonded to the right is a C atom with a double bonded O atom above and a single bonded O atom to the right. To the right of this last O atom in black is another C atom to which H atoms are bonded above, below and to the right. Both O atoms have two pairs of electron dots.

The functional groups for an acid and for an ester are shown in red in these formulas.

Carboxylic Acids

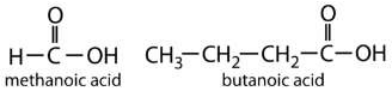
Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure 18.8.1). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



Figure 18.8.2 Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock



The carboxyl group contains the C=O of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (–OH) group. A **carboxylic acid** is an organic compound that contains the carboxyl functional group. The general formula for a carboxylic acid can be abbreviated as R–COOH. The carbon atom of the carboxyl group may be attached to a hydrogen atom or to a carbon chain. The naming of a carboxylic acid is as follows: Name the parent compound by finding the longest continuous chain that contains the carboxyl group. Change the *-e* at the end of the name of the alkane to *-oic acid*.



Carboxylic acids are weak acids, meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:

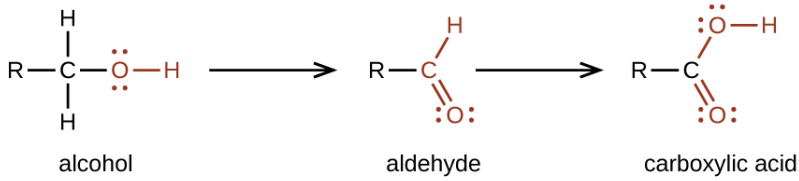
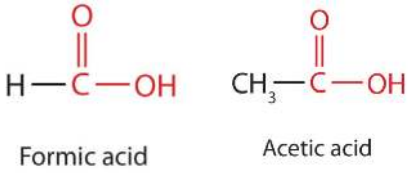


Figure **18.8.3** A chemical reaction with two arrows is shown. On the left, an alcohol, indicated with a C atom to which an R group is bonded to the left, H atoms are bonded above and below, and in red, a single bonded O atom with an H atom bonded to the right is shown. Following the first reaction arrow, an aldehyde is shown. This structure is represented with an R group bonded to a red C atom to which an H atom is bonded above and to the right, and an O atom is double bonded below and to the right. Appearing to the right of the second arrow, is a carboxylic acid comprised of an R group bonded to a C atom to which, in red, an O atom is single bonded with an H atom bonded to its right side. A red O is double bonded below and to the right. All O atoms have two pairs of electron dots.

The simplest carboxylic acid, formic acid (HCOOH, methanoic acid), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).

The next higher homolog is acetic acid (CH_3COOH, ethanoic acid), which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often “froze” on the storage shelf. For that reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid (CH_3CH_2COOH, propionic acid), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives.

Many carboxylic acids occur naturally in plants and animals. Citrus fruits such as oranges and lemons contain citric acid (Figure **18.8.4**). Ethanoic and citric acids are frequently added to foods to give them a tart flavor.

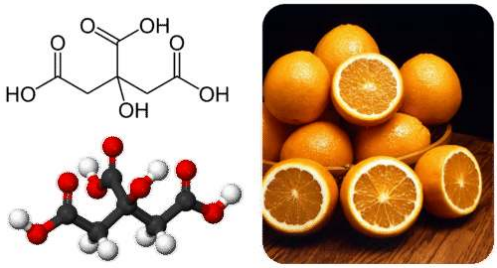
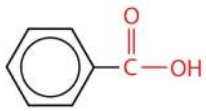


Figure **18.8.4**: Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

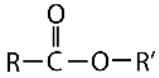
Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives, and coatings.



Benzoic acid

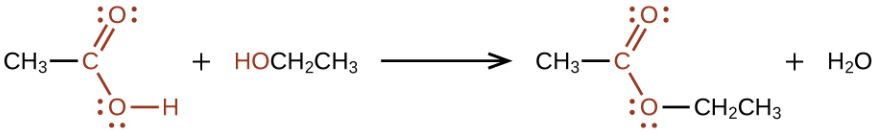
Esters: The Sweet Smell of RCOOR'

An **ester** is an organic compound that is a derivative of a carboxylic acid in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group. The structure is the product of a carboxylic acid (the **R**-portion) and an alcohol (the **R′**-portion). The general formula for an ester is shown below.



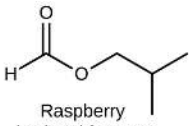
The **R** group can either be a hydrogen or a carbon chain. The **R′** group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid.

Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $CH_3CO_2CH_2CH_3$, is formed when acetic acid reacts with ethanol:

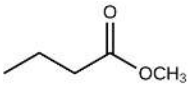


acetic acid ethanol ethyl acetate

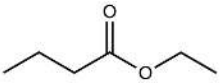
Figure **18.8.5**). Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.A chemical reaction is shown. On the left, a C H subscript 3 group bonded to a red C atom. The C atom forms a double bond with an O atom which is also in red. The C atom is also bonded to an O atom which is bonded to an H atom, also in red. A plus sign is shown, which is followed by H O C H subscript 2 C H subscript 3. The H O group is in red. Following a reaction arrow, a C H subscript 3 group is shown which is bonded to a red C atom with a double bonded O atom and a single bonded O. To the right of this single bonded O atom, a C H subscript 2 C H subscript 3 group is attached and shown in black. This structure is followed by a plus sign and H subscript 2 O. The O atoms in the first structure on the left and the structure following the reaction arrow have two pairs of electron dots.



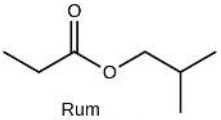
Raspberry
iso-butyl formate



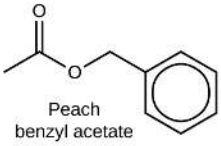
Apple
butyl acetate



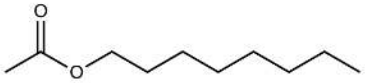
Pineapple
ethyl butyrate



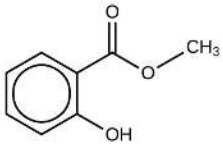
Rum
propyl isobutyrate



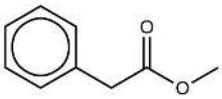
Peach
benzyl acetate



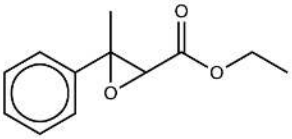
Orange
octyl acetate



Wintergreen
methyl salicylate



Honey
methyl phenylacetate



Strawberry
ethyl methylphenylglycidate

Figure **18.8.6** Esters are responsible for the odors associated with various plants and their fruits. There are nine structures represented in this figure. The first is labeled, “raspberry,” and, “iso-butyl formate.” It shows an H atom with a line going up and to the right which then goes down and to the right. It goes up and to the right again and down and to the right and up and to the right. At the first peak is a double bond to an O atom. At the first trough is an O atom. At the second trough, there is a line going straight down. The second is labeled, “apple,” and, “butyl acetate.” There is a line that goes up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom. At the end, on the right is O C H subscript 3. The third is labeled, “pineapple,” and, “ethyl butyrate.” It is a line that goes up and to the right, down and to the right, up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom and at the second trough is an O atom. The fourth is labeled, “rum,” and “propyl isobutyrate.” It shows a line that goes down and to the right, up and to the right, down and to the right, up and to the right, down and to the right and up and to the right. The first complete peak has a double bond to an O atom and the second trough has an O atom. The fifth is labeled, “peach,” and “benzyl acetate.” It shows a line that goes up and to the right, down and to the right, up and to the right and down and to the right. This line connects to a hexagon with a circle inside it. The first peak has a double bond to an O atom and the first trough has an O atom. The sixth is labeled, “orange,” and, “octyl acetate.” It shows a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. The first peak has a double bond to an O atom and the first complete trough has and an O atom. The seventh is labeled, “wintergreen,” and “methyl salicylate.” It shows a hexagon with a circle inside of it. On the right, is a bond down and to the right to an O H group. On the right is a bond to a line that goes up and to the right and down and two the right and up and to the right. At the first peak is a double bond to an O atom, the next trough shows and O atom and at the end of the line is a C H subscript 3 group. The eighth is labeled, “honey,” and “methyl phenylacetate.” It shows a hexagon with a circle inside of it. It shows it connecting to a line on the right that goes down and to the right then up and to the right and down and to the right and up and to the right. At the first peak that is not part of the hexagon is a double bond to an O atom. At the last trough is an O atom. The ninth is labeled, “strawberry,” and “ethyl methylphenylglycidate.” This shows a hexagon with a circle inside of it. On the right, it connects to a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. At the first peak is a line that extends above and below. Below, it connects to an O atom. At the next trough, the line extends down and to the left to the same O atom. At the next peak is a double bond to an O atom and at the next trough is an O atom.

Chemistry Is Everywhere: Esters, Fragrances, and Flavorings

Esters are very interesting compounds, in part because many have very pleasant odors and flavors. (Remember, never taste anything in the chemistry lab!) Many esters occur naturally and contribute to the odor of flowers and the taste of fruits. Other esters are synthesized industrially and are added to food products to improve their smell or taste; it is likely that if you eat a product whose ingredients include artificial flavorings, those flavorings are esters. Here are some esters and their uses, thanks to their odors, flavors, or both:

Table **18.8.1**: Esters, Fragrances, and Flavorings

Ester	Tastes/Smells Like	Ester	Tastes/Smells Like
allyl hexanoate	pineapple	isobutyl formate	raspberry
benzyl acetate	pear	isobutyl acetate	pear
butyl butanoate	pineapple	methyl phenylacetate	honey
ethyl butanoate	banana	nonyl caprylate	orange
ethyl hexanoate	pineapple	pentyl acetate	apple
ethyl heptanoate	apricot	propyl ethanoate	pear
ethyl pentanoate	apple	propyl isobutyrate	rum

Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $C_3H_5(OH)_3$, with large carboxylic acids, such as palmitic acid, $CH_3(CH_2)_{14}CO_2H$, stearic acid, $CH_3(CH_2)_{16}CO_2H$, and oleic acid, $\mathbf{CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H}$. Oleic acid is an unsaturated acid; it contains a $\mathbf{C=C}$ double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

Note

Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Summary

- A carboxylic acid is an organic compound that contains the carboxyl functional group.
- The general formula for a carboxylic acid can be abbreviated as $\mathbf{R{-}COOH}$.
- Many carboxylic acids are used in the food and beverage industry for flavoring and/or as preservatives.
- An ester has an OR group attached to the carbon atom of a carbonyl group.
- Fats and vegetable oils are esters of long-chain fatty acids and glycerol.
- Esters occur widely in nature and generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers.

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18.9: Nitrogen-Containing Compounds- Amines and Amides

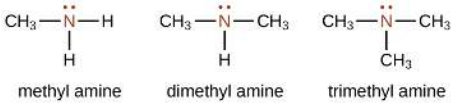
Learning Objectives

- Describe the structure and properties of amines and amides.
- Name simple amines and amides.

The addition of nitrogen into an organic framework leads to two families of molecules. Compounds containing a nitrogen atom bonded in a hydrocarbon framework are classified as amines. Compounds that have a nitrogen atom bonded to one side of a carbonyl group are classified as amides.

Amines

An **amine** is an organic compound that can be considered to be a derivative of ammonia (NH_3). Amines are molecules that contain carbon-nitrogen bonds. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine* as illustrated here for a few simple examples:



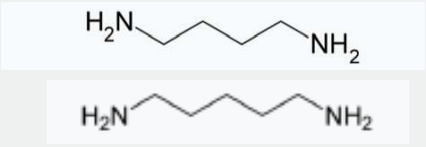
The name of larger molecules involve the class-identifying suffix *–ine* as you will see later in this section(e.g. caffeine and nicotine).

Methylamine and ethylamine are gases at room temperature, while larger amines are liquids. As with other organic compounds that form hydrogen bonds, water solubility is reflected in the length of the carbon chains. Smaller amines are soluble, while larger ones are less soluble.

Amines generally have rather pungent or noxious odors. Ammonia can be considered the simplest amine and has a very distinctive odor. Methylamine has an unpleasant odor associated with dead fish. Amines are often formed biologically during the breakdown of proteins in animal cells, and so many have the smell of death and decay. Putrescine and cadaverine are two such amines and are aptly named for their foul odors. The toxins which many animals use as a form of defense are frequently amines. Amines are used industrially as dyes and in many drugs.

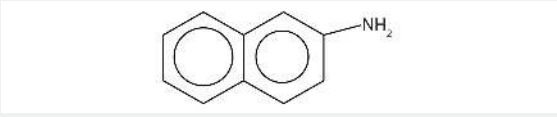
To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



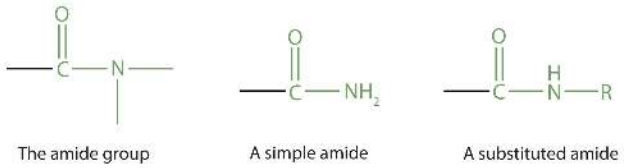
(Figure 18.9.1) Putrescine(left) Cadaverine (right)

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Amides

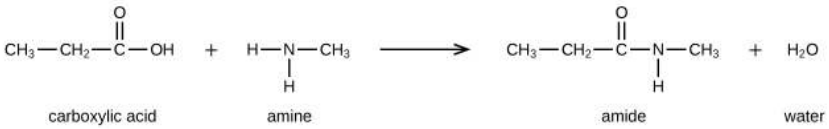
The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound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



Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation. A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the previous section):



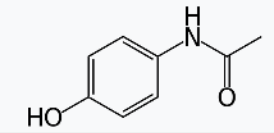
(Figure **18.9.2**) reaction between carboxylic acid and amine to form amide and water

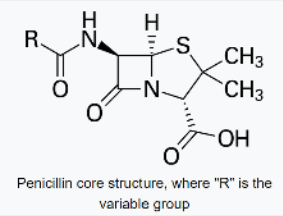
The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

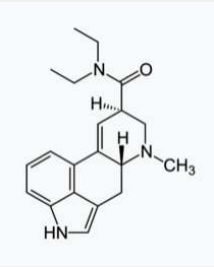
> The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Amides are pervasive in nature and technology as structural materials. The amide linkage is easily formed, confers structural rigidity, and resists hydrolysis. Nylons are polyamides, as are the very resilient materials Aramid, Twaron, and Kevlar. Amide linkages constitute a defining molecular feature of proteins, the secondary structure of which is due in part to the hydrogen bonding abilities of amides. Amide linkages in a biochemicalcontext are called peptide bonds when they occur in the main chain of a protein and isopeptide bonds when they occur to a side-chain of the protein. Proteins can have structural roles, such as in hair or spider silk, but also nearly all enzymes are proteins. Low molecular weight amides, such as dimethylformamide ($HC(O)N(CH_3)_2$), are common solvents. Many drugs are amides, including paracetamol, penicillin and LSD. Moreover, plant *N*-alkylamides have a wide range of biological functionalities.

Drugs with the Amide Group







(Figure 18.9.3) Paracetamol (acetaminophen) LSD (Lysergic diethylamide)

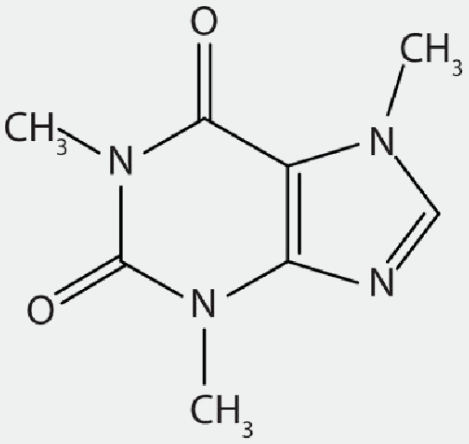
Heterocyclic Compounds: Alkaloids and Others

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning "other"), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

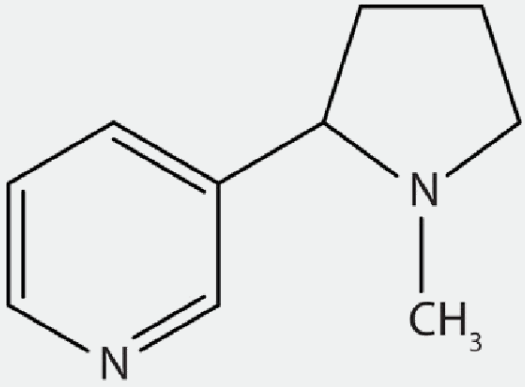
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



Caffeine

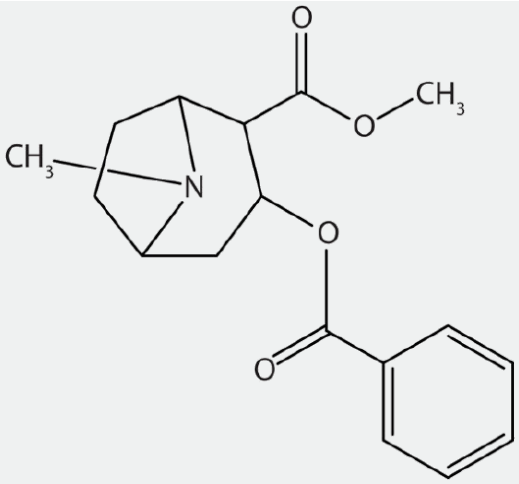
Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.



Cocaine

$$C_{17}H_{21}O_4N + HCl \longrightarrow C_{17}H_{21}O_4NH^+Cl^-$$

Cocaine (freebase) → Cocaine hydrochloride

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

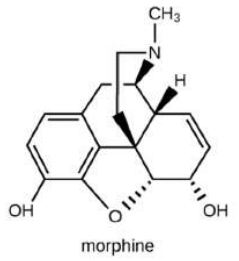
Morphine and Heroin

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

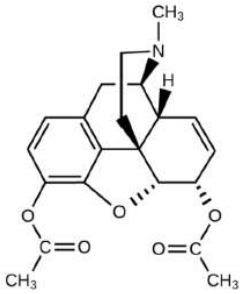


Figure **18.9.4** Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

molecule in this structural formula. Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic. If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results (Figure **18.9.4**).



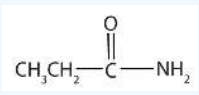
morphine

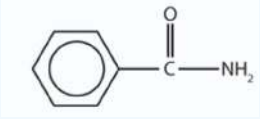


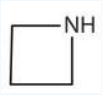
heroin

Example 18.9.1: Amines and Amides

Identify whether each compound is an amide or an amine.

a. 

b. 

c. 

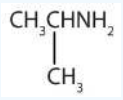
Solutions

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

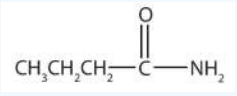
b. The compound has the $CONH_2$ functional group so it is an amide.

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

? Exercise 18.9.1

a. 

b. $CH_3CH_2CH_2CH_2CH_2CH_2NH_2$

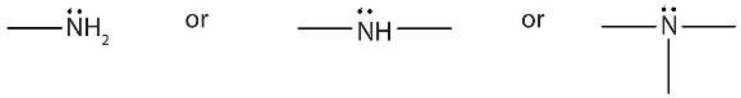
c. 

Answer

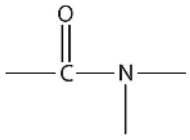
a. amine b. amine c. amide

Summary

- An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The



amine functional group is as follows:
- Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.
- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.



(Figure **18.9.5**) Amide

- Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:
- Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

Contributors and Attributions

Marisa Alviar-Agnew (Sacramento City College)

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

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CHAPTER OVERVIEW

19: Biochemistry

19.1: Energy and the Living Cell
19.2: Carbohydrates- A Storehouse of Energy
19.3: Fats and Other Lipids
19.4: Proteins- Polymers of Amino Acids
19.5: Structure and Function of Proteins
19.6: Membranes and Membrane Lipids
19.7: Nucleotides
19.8: Nucleic Acids- Parts, Structure, and Function
19.9: RNA Protein Synthesis and the Genetic Code
19.10: Viruses
19.E: Nucleic Acids (Exercises)
19.S: Amino Acids, Proteins, and Enzymes (Summary)
19.S: Nucleic Acids (Summary)

Thumbnail: DNA double helix. (public domain; NIH - Genome Research Institute).

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19.1: Energy and the Living Cell

Learning Objective

- Know the similarities and differences between plant and animal cells.
- Know the functions of the major parts of plant and animal cells.

Biochemistry, sometimes called **biological chemistry**, is the study of chemical processes within and relating to living organisms. Biochemical processes give rise to the complexity of life. Biochemistry focuses on understanding how biological molecules give rise to the processes that occur within living cells and between cells, which in turn relates greatly to the study and understanding of tissues, organs, and organism structure and function. Much of biochemistry deals with the structures, functions and interactions of biological macromolecules, such as proteins, nucleic acids, carbohydrates and lipids, which provide the structure of cells and perform many of the functions associated with life. The mechanisms by which cells harness energy from their environment via chemical reactions are known as metabolism. The findings of biochemistry are applied primarily in medicine, nutrition, and agriculture. In medicine, biochemists investigate the causes and cures of diseases. In nutrition, they study how to maintain health wellness and study the effects of nutritional deficiencies. In agriculture, biochemists investigate soil and fertilizers, and try to discover ways to improve crop cultivation, crop storage and pest control.

The major parts of plant and animal cells (Figure 19.1.1) include the plasma membrane, nucleus, ribosomes, and mitochondria.

The plasma membrane is made up of a phospholipid bilayer with embedded proteins that separates the internal contents of the cell from its surrounding environment. A phospholipid is a lipid molecule composed of two fatty acid chains, a glycerol backbone, and a phosphate group. The plasma membrane regulates the passage of some substances, such as organic molecules, ions, and water, preventing the passage of some to maintain internal conditions, while actively bringing in or removing others. Other compounds move passively across the membrane.

Nucleus

Typically, the **nucleus** is the most prominent organelle in a cell . The nucleus (plural = nuclei) houses the cell's DNA in the form of chromatin and directs the synthesis of ribosomes and proteins.

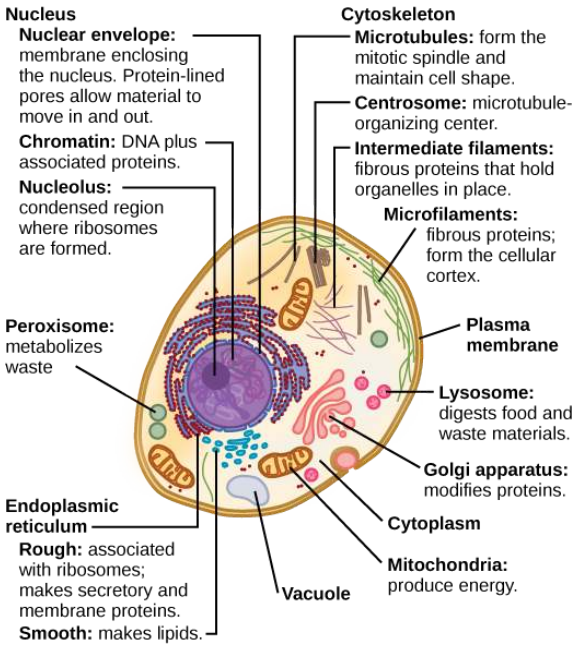
Ribosomes

Ribosomes are the cellular structures responsible for protein synthesis. When viewed through an electron microscope, free ribosomes appear as either clusters or single tiny dots floating freely in the cytoplasm. Ribosomes may be attached to either the cytoplasmic side of the plasma membrane or the cytoplasmic side of the endoplasmic reticulum. Electron microscopy has shown that ribosomes consist of large and small subunits. Ribosomes are enzyme complexes that are responsible for protein synthesis.

Because protein synthesis is essential for all cells, ribosomes are found in practically every cell, although they are smaller in prokaryotic cells. They are particularly abundant in immature red blood cells for the synthesis of hemoglobin, which functions in the transport of oxygen throughout the body.

Mitochondria

Mitochondria (singular = mitochondrion) are often called the "powerhouses" or "energy factories" of a cell because they are responsible for making adenosine triphosphate (ATP), the cell's main energy-carrying molecule. The formation of ATP from the breakdown of glucose is known as cellular respiration. In keeping with our theme of form following function, it is important to point out that muscle cells have a very high concentration of mitochondria because muscle cells need a lot of energy to contract.



(a)

Figure_03_03_01b_new.png?revision=1&size=bestfit&width=519&height=476" style="width: 490.994px; height: 450px;" />

Figure* 19.1.1*: *This figure shows (a) a typical animal cell and (b) a typical plant cell.*

Animal Cells versus Plant Cells

Despite their fundamental similarities, there are some striking differences between animal and plant cells. Animal cells have centrioles, centrosomes (discussed under the cytoskeleton), and lysosomes, whereas plant cells do not. Plant cells have a cell wall (made of cellulose), chloroplasts, plasmodesmata, and plastids used for storage, and a large central vacuole, whereas animal cells do not.

Energy in Biological Systems

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{19.1.1}$$

(The 686 kcal come from solar energy.) Chloroplasts function in photosynthesis and can be found in cells of plants and algae. The chloroplasts contain a green pigment called chlorophyll, which captures the energy of sunlight for photosynthesis. Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids. This is the major difference between plants and animals: Plants are able to make their own food, like glucose, whereas animals must rely on other organisms for their organic compounds or food source.

Summary

The major parts of plant and animal cells (Figure **19.1.1**) include the plasma membrane, nucleus, ribosomes, and mitochondria.

Animal cells have centrioles, centrosomes (discussed under the cytoskeleton), and lysosomes, whereas plant cells do not.

Plant cells have a cell wall (made of cellulose), chloroplasts, plasmodesmata, and plastids used for storage, and a large central vacuole, whereas animal cells do not.

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis.

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- Wikipedia
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19.2: Carbohydrates- A Storehouse of Energy

Learning Objective

- Know the difference between starch, cellulose and glycogen.
- List the key steps in carbohydrate digestion.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. Different carbohydrates that will be discussed below include the simple sugars, oligosaccharides and polysaccharides (Figure **19.2.1**.

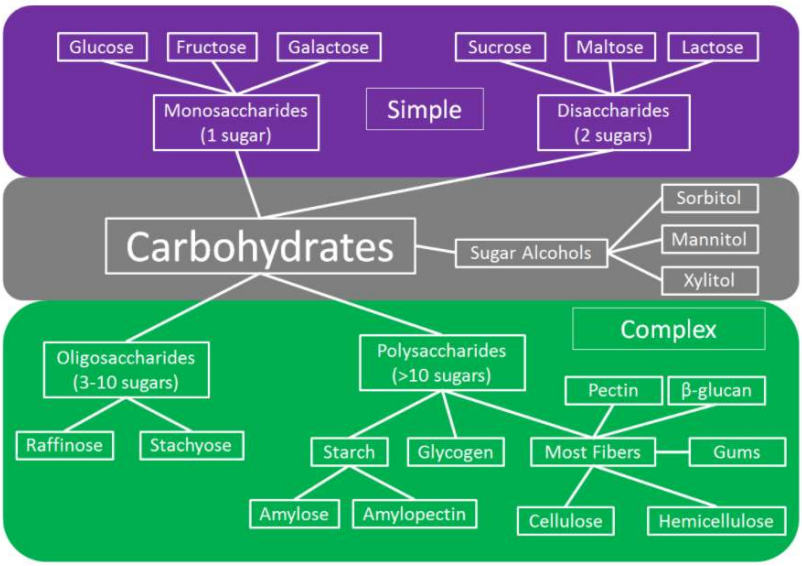
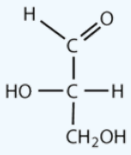
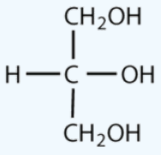


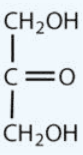
Figure **19.2.1** *Overview of carbohydrates*

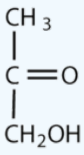
Example 19.2.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.

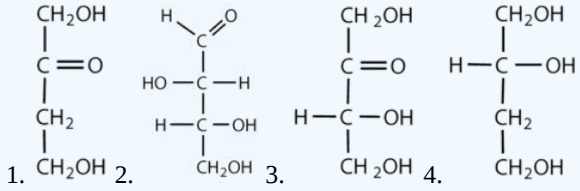
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

? Exercise 19.2.1

Which compounds would be classified as carbohydrates?



Some Simple Sugars

The naturally occurring **monosaccharides** contain three to seven carbon atoms per molecule (one sugar unit) . Monosaccharides (or simple sugars) of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **19.2.2**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

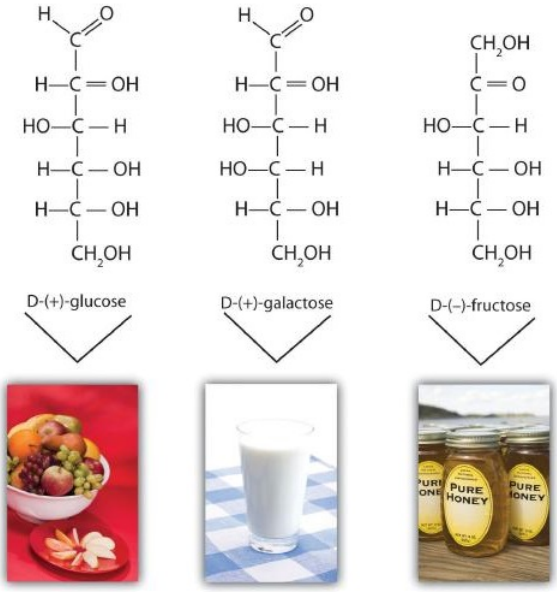


Figure **19.2.2**: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure. The representative ring structures of glucose, fructose, and galactose are shown in Figure **19.2.3**. Notice that all are 6-carbon sugars (hexoses). However, fructose has a five member ring, while glucose and galactose have 6 member rings. Also notice that the only structural difference between glucose and galactose is the position of the alcohol (OH) group that is shown in red.

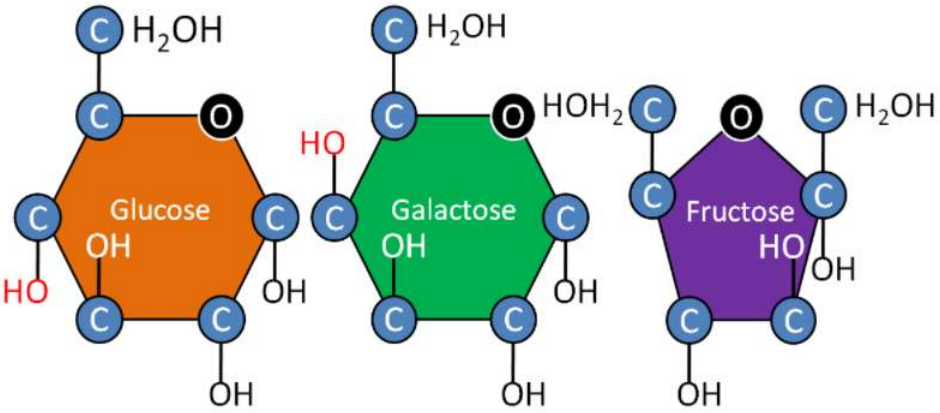


Figure **19.2.3** *The ring structures of glucose, galactose, and fructose.*

A **disaccharide** contains two monosaccharides joined together. Examples include and . They are composed of two monosaccharide units bound together by a bond known as a formed via a , resulting in the loss of a atom from one monosaccharide and a from the other. The of unmodified disaccharides is $C_{12}H_{22}O_{11}$. Although there are numerous kinds of disaccharides, a handful of disaccharides are particularly notable.

Sucrose, which may be obtained by condensing a molecule of α-glucose with one of the cyclic forms of fructose called β-fructose. The structure of sucrose is shown in Figure **19.2.4**.

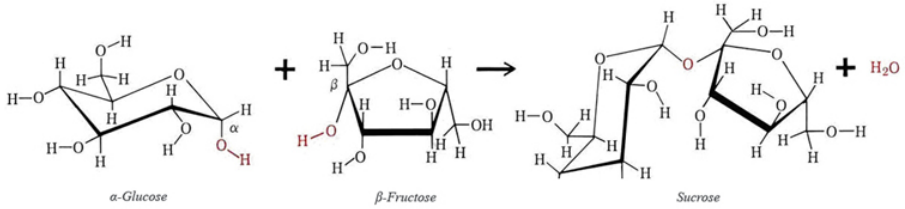


Figure **19.2.4** *The formation of sucrose from glucose and fructose.*

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure **19.2.5**. In order to digest a disaccharide like sucrose or lactose, the human body must have an enzyme which can catalyze hydrolysis of the linkage between the two monosaccharide units. Many Asians, Africans, and American Indians are incapable of synthesizing lactase, the enzyme that speeds hydrolysis of lactose. If such persons drink milk, the undigested lactose makes them sick.

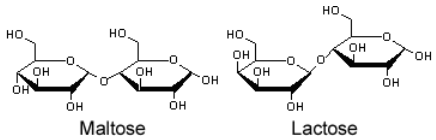


Figure **19.2.5** Two other common disaccharides, maltose and lactose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of

reduced photosynthetic activity. We often think of potatoes as a “starchy” food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure **19.2.6**). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure **19.2.6**). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

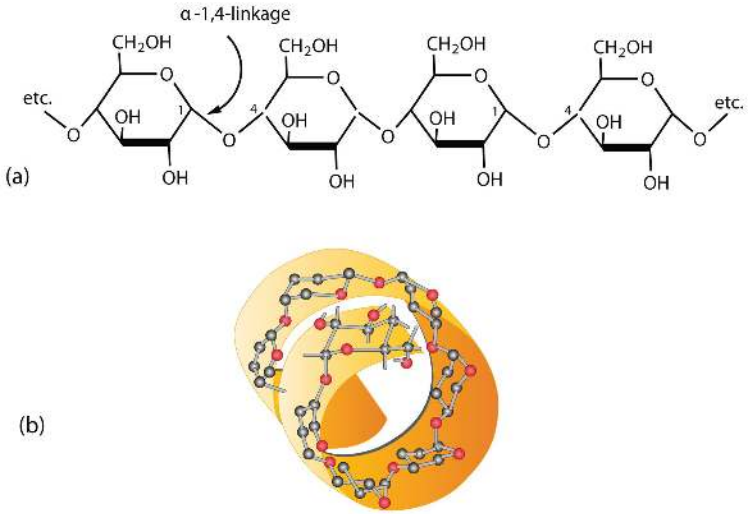


Figure **19.2.6** Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure **19.2.7**). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

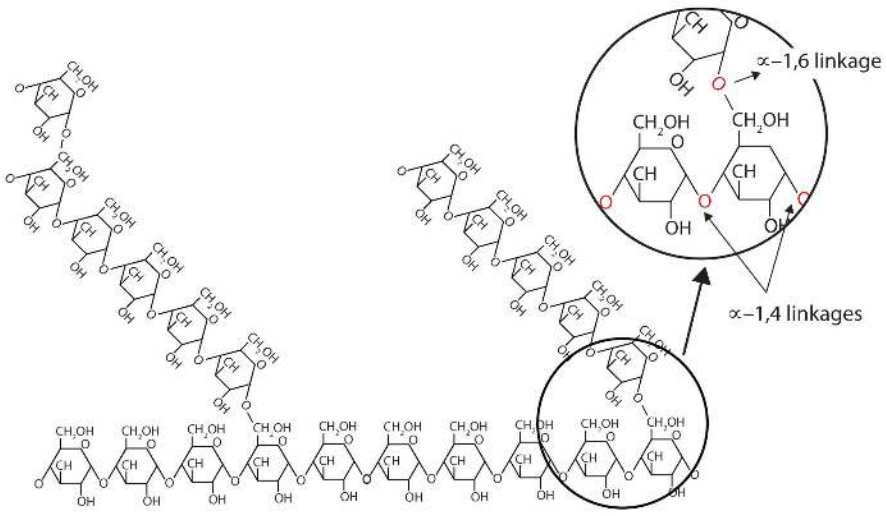


Figure **19.2.7** Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> *About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.*

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure **19.2.8**). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure **19.2.8**). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

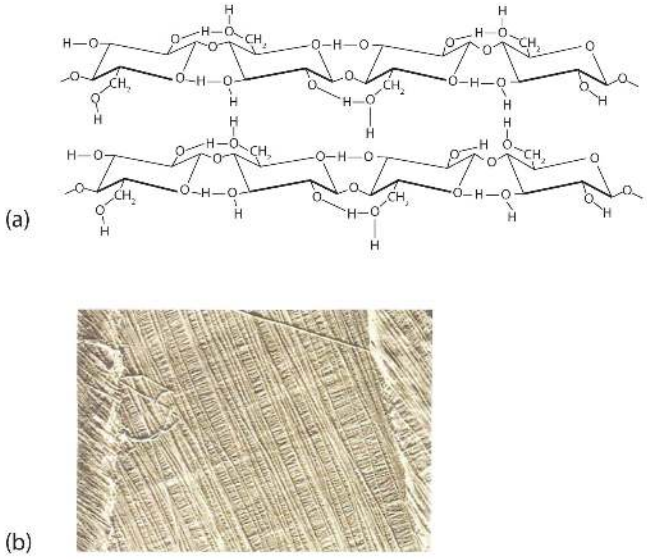


Figure **19.2.8** Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Summary

- Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched).
- Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin.
- Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

Sources

Wikipedia

Contributors and Attributions

- Template:ContribLindshield
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19.3: Fats and Other Lipids

Learning Objectives

- Recognize the structures of common fatty acids.
- Describe the structure of fats and oils and classify them as saturated, monounsaturated, or polyunsaturated.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure **19.3.1** presents one scheme for classifying the various kinds of lipids). We will discuss the various kinds of lipids by considering one subclass at a time and pointing out structural similarities and differences as we go.

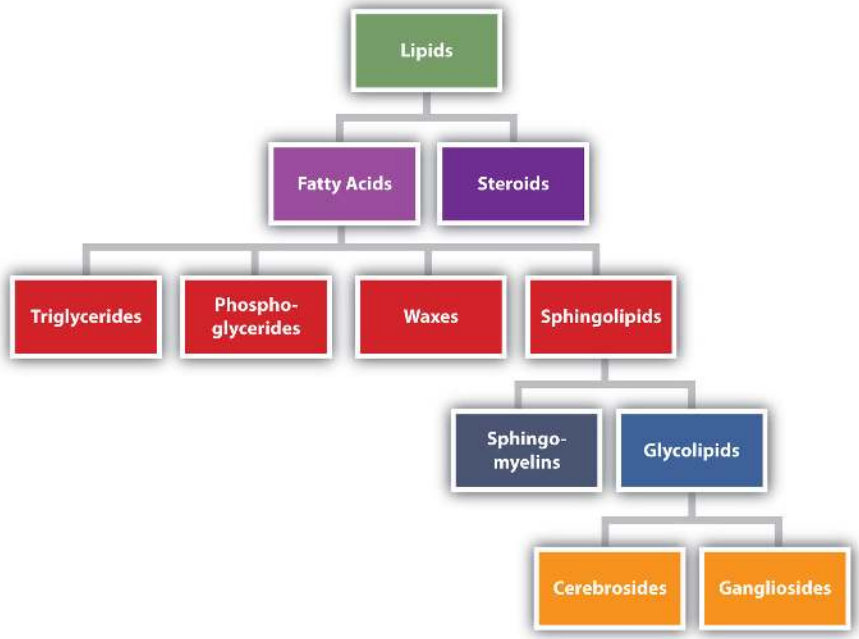


Figure **19.3.1** *Lipid organization based on structural relationships*

Fatty Acids

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids

contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.

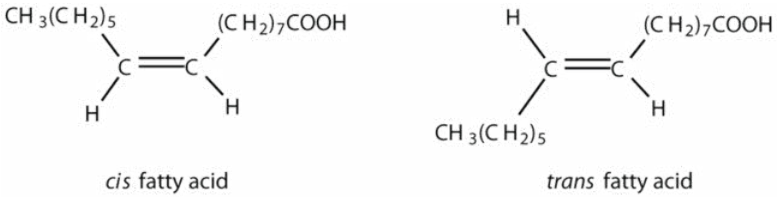


Table **19.3.1** lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table **19.3.1** Some Common Fatty Acids Found in Natural Fats.

Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	olive oil
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	−5	canola oil
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	−11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$	−50	liver

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood. Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure **19.3.2*a***). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure **19.3.2*b***). Such molecules pack closely together into a crystal lattice, maximizing the strength of dispersion forces and causing fatty acids and the fats derived from them to have relatively high melting points. In contrast, each *cis* carbon-to-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the intermolecular attractions of unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most are liquids at room temperature.

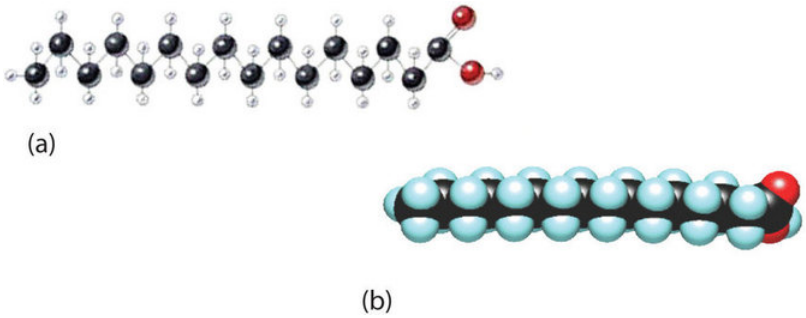
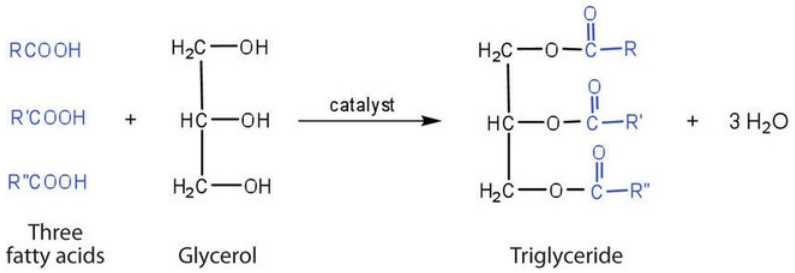


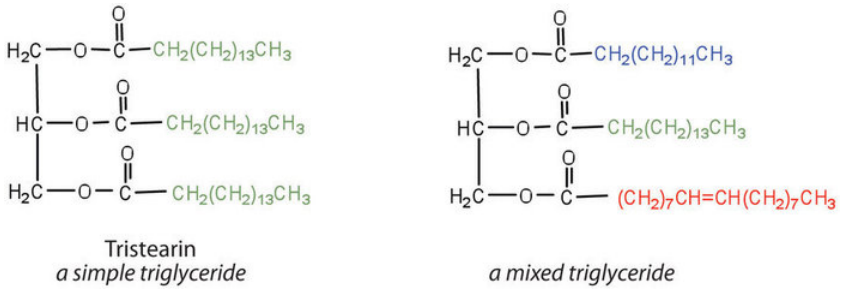
Figure **19.3.2** The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Structures of Fats and Oils

Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table **19.3.2** shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

Table **19.3.2** Average Fatty Acid Composition of Some Common Fats and Oils (%)*.

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil†	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

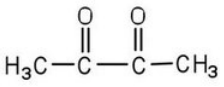
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

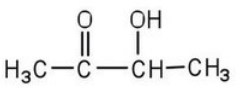
Terms such as ***saturated fat*** or *unsaturated oil* are often used to describe the fats or oils obtained from foods. **Saturated fats** contain a high proportion of saturated fatty acids, while **unsaturated oils** contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Physical Properties of Fats and Oils

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



Diacetyl

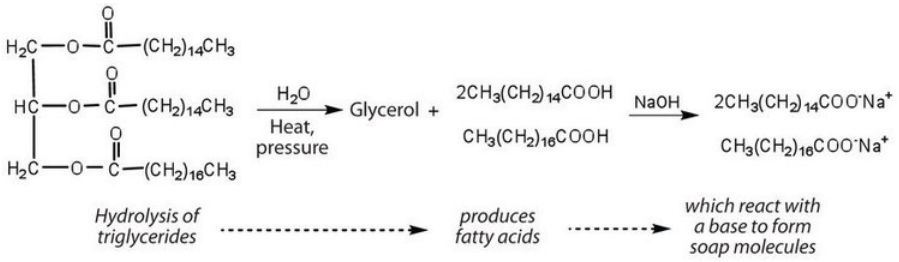


3-hydroxy-2-butanone

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):



Iodine Value

The **iodine value** (or **iodine adsorption value** or **iodine number** or **iodine index**, commonly abbreviated as **IV**) in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine numbers are often used to determine the amount of unsaturation in fats, oils and waxes. In fatty acids, unsaturation occurs mainly as double bonds which are very reactive towards halogens, the iodine in this case. Thus, the higher the iodine value, the more unsaturations are present in the fat. It can be seen from the table that coconut oil is very saturated, which means it is good for making soap. On the other hand, linseed oil is highly unsaturated, which makes it a drying oil, well suited for making oil paints.

Table **19.3.1** *Iodine Numbers of Common Fats and Oils. Source Wikipedia*

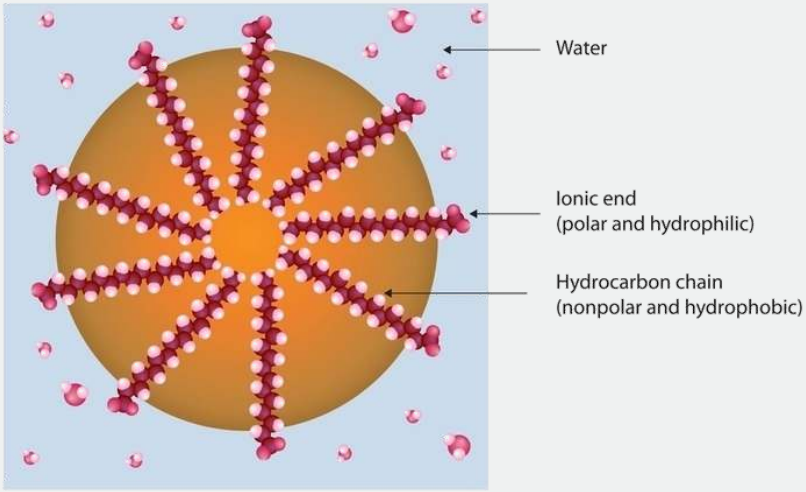
Fat	Iodine Value (g/100g)
Beef tallow	42-48
Butter	25-42
Canola Oil	110-126
Coconut Oil	6-11
Fish oil	190-205
Linseed Oil	170-204
Olive Oil	75-94
Safflower Oil	135-150
Walnut Oil	132-162

Looking Closer: Soaps

Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.

Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon



structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer "gluing" the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

Summary

- Fatty acids are carboxylic acids that are the structural components of many lipids.
- Saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.
- Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol.
- Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases.
- The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification.
- Animal fats and oils which are made up mostly of saturated fatty acids have low iodine values (numbers), while those oils with high degree of unsaturation (with more C=C bonds) have high iodine values.

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19.4: Proteins- Polymers of Amino Acids

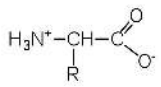
Learning Objectives

- Identify different amino acids.
- Describe how short chain proteins (polypeptides) are formed from amino acids.

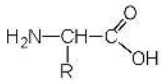
Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion

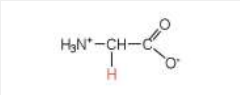
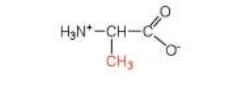
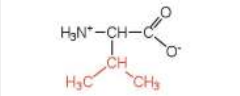
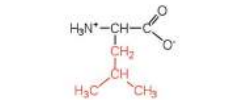
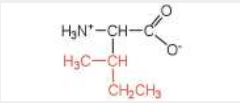
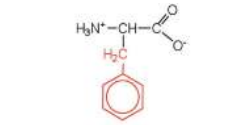
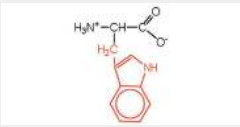
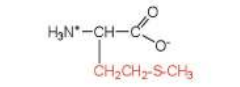
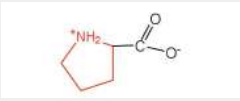
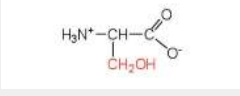
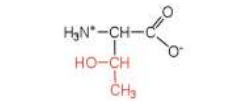
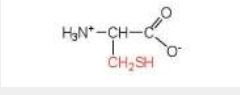


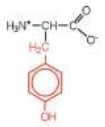
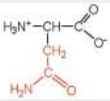
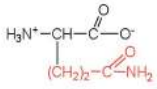
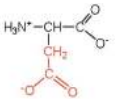
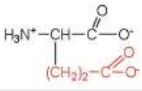
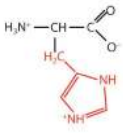
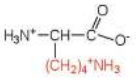
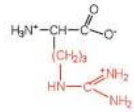
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

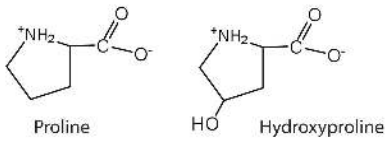
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table **19.4.1**.

Table **19.4.1**: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

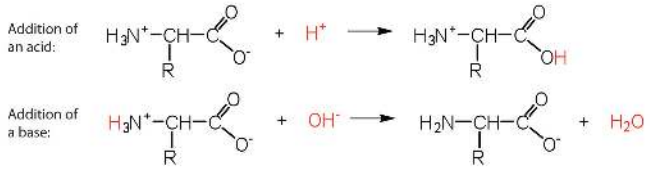
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Zwitterions

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.



The Peptide Bond: Peptides and Proteins

Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage as shown in Figure **19.4.1**

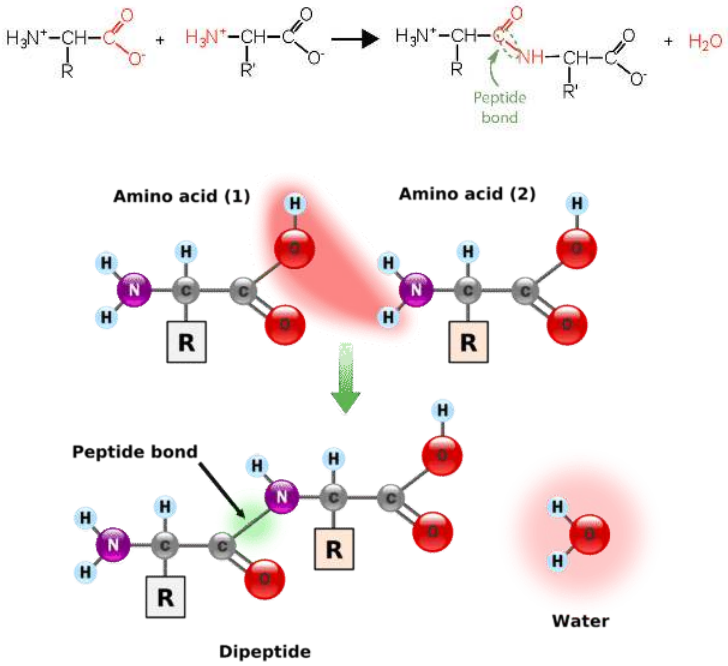
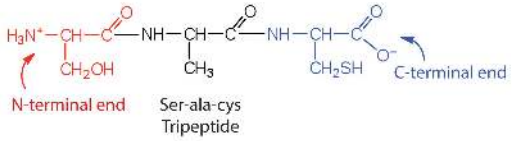


Figure **19.4.1** *Amino acids undergo condensation to form a molecule called a dipeptide. The* **C–N** *bond is called a peptide bond.*

An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.

A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.

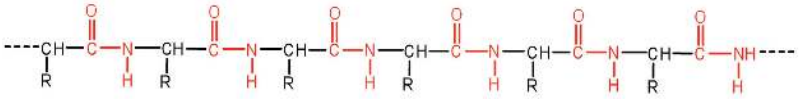


The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

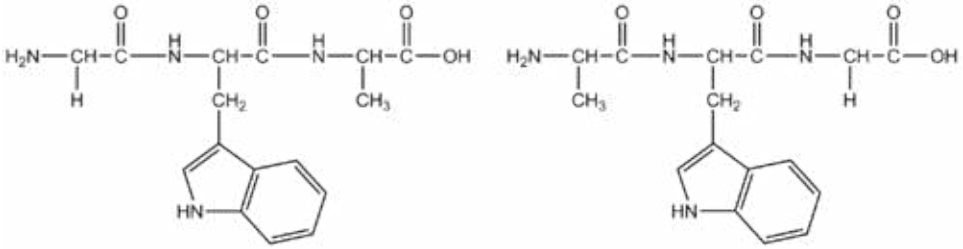
Peptide cells in our bodies have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to synthesize the same proteins in a lab. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react and the amino acid sequence must be a specific one in order for the protein to function. Robert Merrifield developed the first synthetic approach for making proteins in the lab, a manual approach which was lengthy and tedious (and, he won the Nobel Prize in Chemistry in 1984 for his work). Today, however, automated systems can crank out a peptide in a very short period of time.

The Sequence of Amino Acids

The particular sequence of amino acids in a longer chain is called an amino acid sequence. By convention, the amino acid sequence is listed in the order such that the free amine group is on the left end of the molecule and the free carboxyl group is on the right end of the molecule.



For example, suppose that a sequence of the amino acids glycine, tryptophan, and alanine is formed with the free amine group as part of the glycine and the free carboxyl group as part of the alanine. The amino acid sequence can be easily written using the abbreviations as Gly-Trp-Ala. This is a different sequence from Ala-Trp-Gly because the free amine and carboxyl groups would be on different amino acids in that case.



Bradykinin

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure **19.4.2**) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

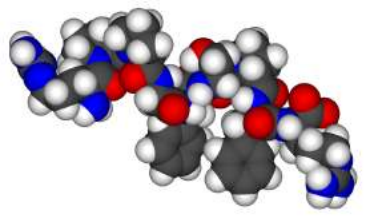


Figure **19.4.2** Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

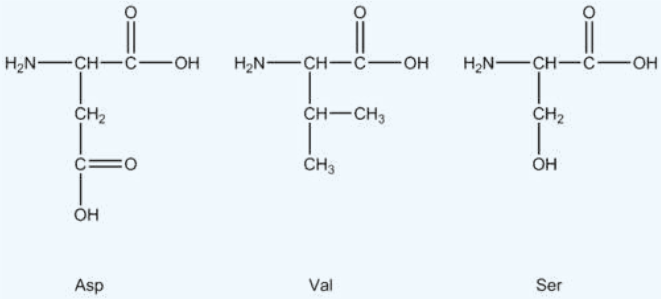
Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of "incorrect" amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That "minor" error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Example 19.4.1

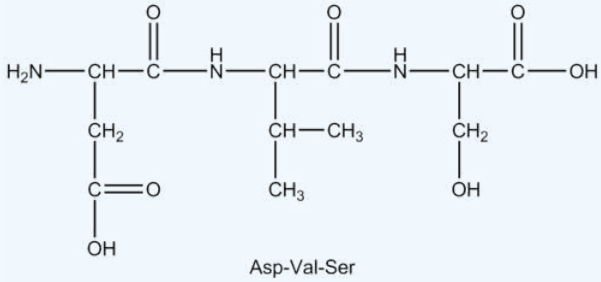
Draw the polypeptide Asp-Val-Ser.

Solution

1. Identify the structures of each of the three given amino acids and draw them in the same order as given in the name.



2. Leaving the order the same, connect the amino acids to one another by forming peptide bonds. Note that the order given in the name is the same way the amino acids are connected in the molecule. The first one listed is always the **N**-terminus of the polypeptide.



Asp-Val-Ser

Example 19.4.2

List all of the possible polypeptides that can be formed from cysteine (Cys), leucine (Leu), and arginine (Arg).

Solution

Although there are only three amino acids, the order in which they are bonded changes the identity, properties, and function of the resulting polypeptide. There are six possible polypeptides formed from these three amino acids.

Cys-Leu-Arg

Cys-Arg-Leu

Leu-Cys-Arg

Leu-Arg-Cys

Arg-Cys-Leu

Arg-Leu-Cys

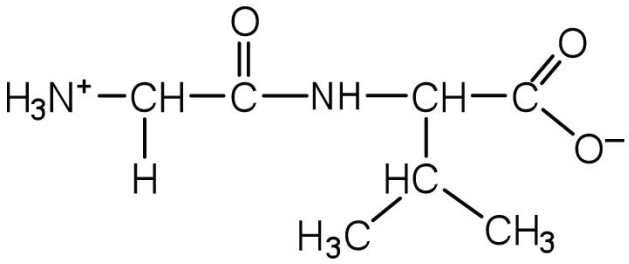
Exercise 19.4.1

Draw the structure for each peptide.

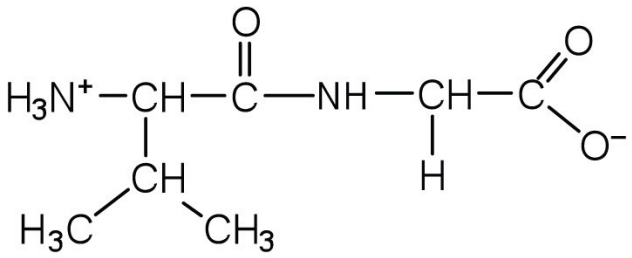
a. gly-val
b. val-gly

Answers

a.



b.



Summary

- The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together.
- Additional amino acids can be added on through the formation of addition peptide (amide) bonds.
- A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*.
- Chains of about 50 amino acids or more are usually called proteins or polypeptides.
- A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).
- The order, or *sequence*, in which the amino acids are connected is also of critical importance in order for a peptide or protein to be physiologically active.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)
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19.5: Structure and Function of Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure
- Explain the role of an enzyme in the body.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the **primary structure**, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure **19.5.1**.

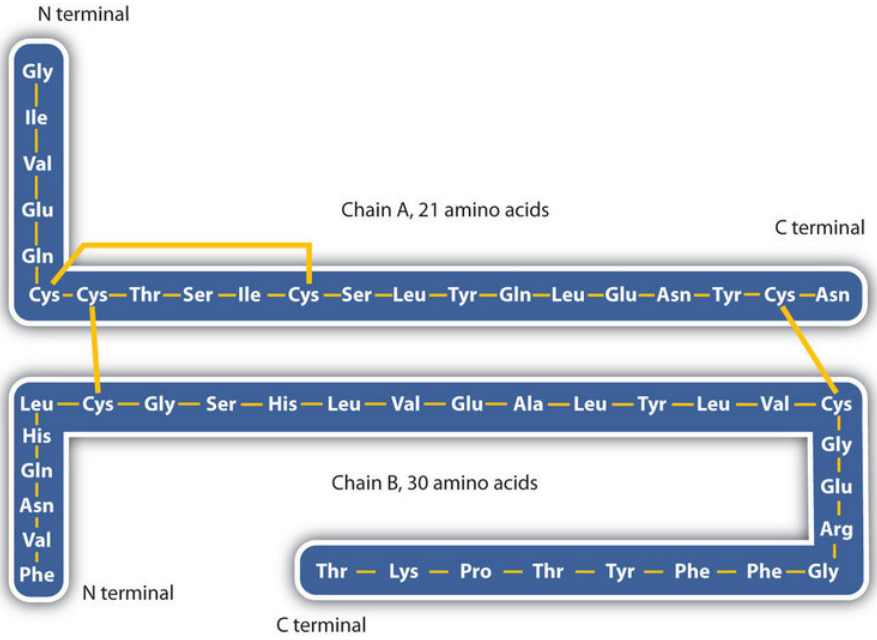


Figure **19.5.1** Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term **secondary structure** refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure **19.5.2**). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

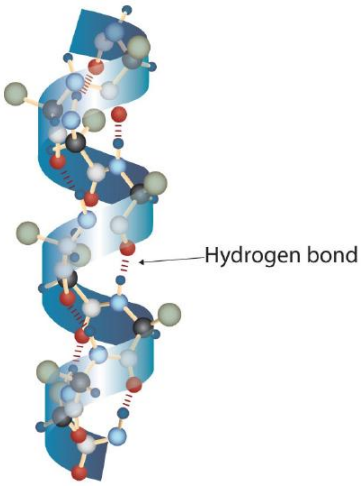


Figure **19.5.2** A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—

and are connected by *interchain* hydrogen bonding (Figure **19.5.3**). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

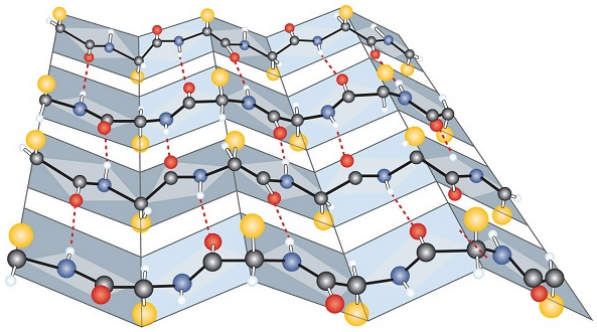


Figure **19.5.3** A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure **19.5.4** shows a depiction of the three-dimensional structure of insulin.

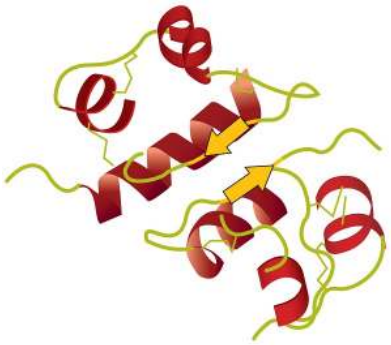
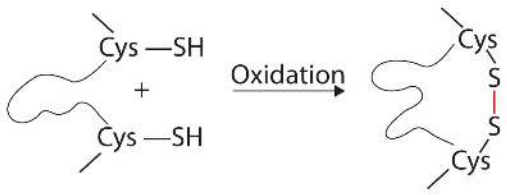


Figure **19.5.4** A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins.

You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure **19.5.5**).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure **19.5.5**).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure **19.5.5**). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure **19.5.1**) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure **19.5.5**). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

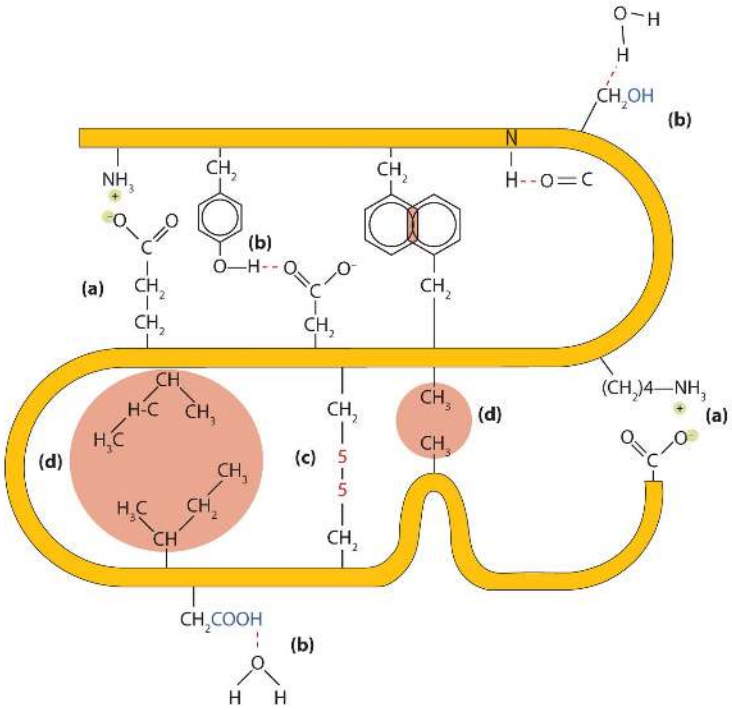


Figure **19.5.5** Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure **19.5.6**). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure **19.5.7**.

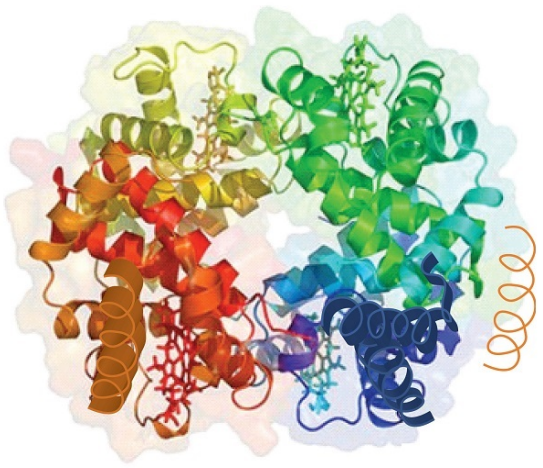


Figure **19.5.6** The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

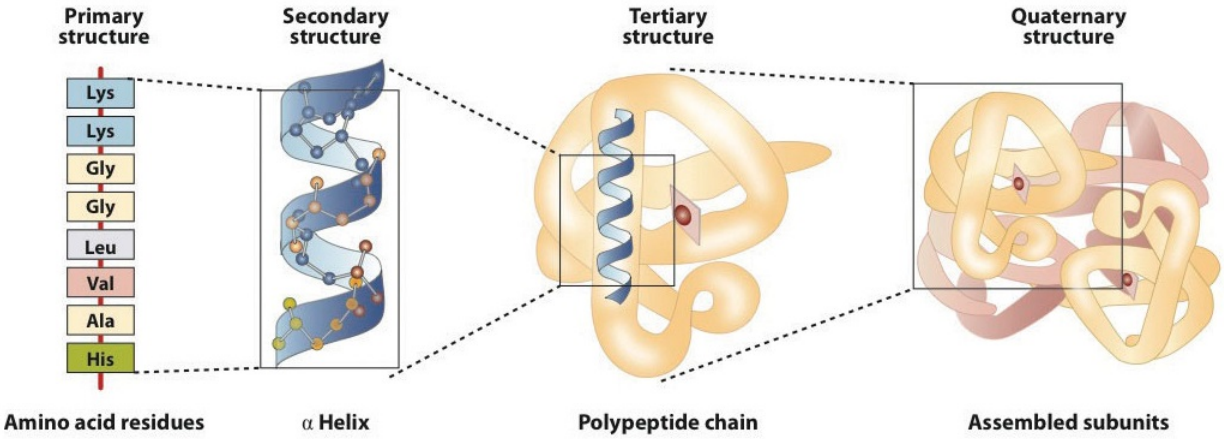


Figure **19.5.7** Levels of Structure in Proteins.

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Globular and Fibrous Proteins

Once proteins form and have developed all levels of their structure, they can be classified as either fibrous or globular. These classifications give the basic shape of the entire protein molecule. While many proteins are **globular proteins** (see figure below), keratin proteins are **fibrous** (see figure below) and make up the hair, nails, and the outer layer of skin.

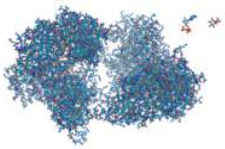


Figure **19.5.8** Globular protein.

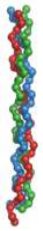


Figure 19.5.9 Fibrous protein.

Enzymes: Exquisite Precision Machines

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$\mathrm{H_2NCON_2}\,(aq) + \mathrm{H_2O}\,(l) \overset{\text{urease}}{\rightarrow} 2\mathrm{NH_3}\,(g) + \mathrm{CO_2}\,(g)$$

His discovery was ridiculed at first because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzymes and Biochemical Reactions

Most chemical reactions within organisms would be impossible under the conditions in cells. For example, the body temperature of most organisms is too low for reactions to occur quickly enough to carry out life processes. Reactants may also be present in such low concentrations that it is unlikely they will meet and collide. Therefore, the rate of most biochemical reactions must be increased by a catalyst. A **catalyst** is a chemical that speeds up chemical reactions. In organisms, catalysts are called **enzymes**. Essentially, enzymes are biological catalysts.

Like other catalysts, enzymes are not reactants in the reactions they control. They help the reactants interact but are not used up in the reactions. Instead, they may be used over and over again. Unlike other catalysts, enzymes are usually highly specific for particular chemical reactions. They generally catalyze only one or a few types of reactions.

Enzymes are extremely efficient in speeding up reactions. They can catalyze up to several million reactions per second. As a result, the difference in rates of biochemical reactions with and without enzymes may be enormous. A typical biochemical reaction might take hours or even days to occur under normal cellular conditions without an enzyme, but less than a second with an enzyme.

Figure 19.5.10 diagrams a typical enzymatic reaction. A **substrate** is the molecule or molecules on which the enzyme acts. In the urease catalyzed reaction, urea is the substrate.

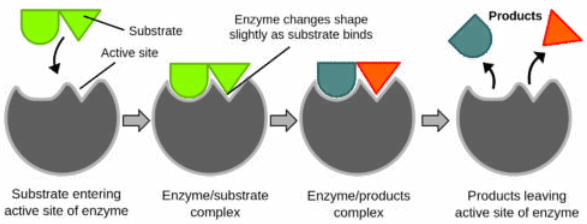


Figure 19.5.10 The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

The first step in the reaction is that the substrate binds to a specific part of the enzyme molecule, known as the active site. The binding of the substrate is dictated by the shape of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the place on an enzyme where the substrate binds. An enzyme folds in such a way that it typically has one active site, usually a pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. In other words, each enzyme catalyzes only one chemical reaction with only one substrate. Once the enzyme/substrate complex is formed, the reaction occurs and the substrate is transformed into products. Finally, the product molecule or molecules

are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

For many enzymes, the active site follows a **lock and key** (Figure 19.5.11*A*) model where the substrate fits exactly into the active site. The enzyme and substrate must be a perfect match so the enzyme only functions as a catalyst for one reaction. Other enzymes have an **induced fit** (Figure 19.5.11*B*) model. In an induced fit model, the active site can make minor adjustments to accommodate the substrate. This results in an enzyme that is capable of interacting with a small group of similar substrates. Look at the shape of the active site compared to the shape of the substrate in B of the figure below. The active site adjusts to accommodate the substrate.

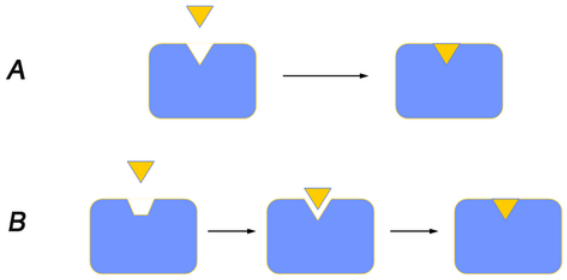


Figure 19.5.11 (A) Lock and key enzyme model and (B) induced fit enzyme model.

Inhibitors

An **inhibitor** is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction. Inhibitors can work in a variety of ways, but one of the most common is illustrated in the figure below.

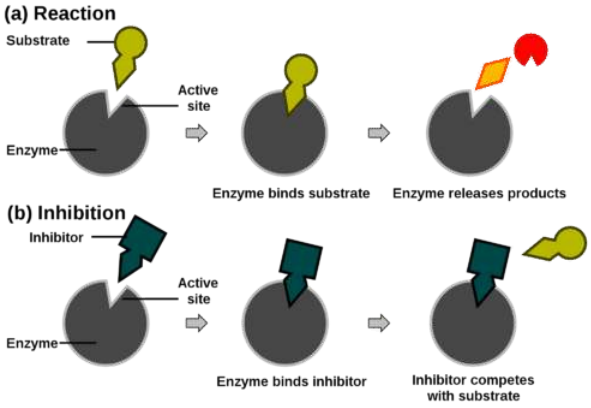


Figure 19.5.12 A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

A **competitive inhibitor** binds competitively at the active site and blocks the substrate from binding. Since no reaction occurs with the inhibitor, the enzyme is prevented from catalyzing the reaction.

A **non-competitive inhibitor** does not bind at the active site. It attaches at an **allosteric site**, which is some other site on the enzyme, and changes the shape of the protein. The allosteric site is any site on the enzyme that is not the active site. The attachment of the non-competitive inhibitor to the allosteric site results in a shift in three-dimensional structure that alters the shape of the active site so that the substrate will no longer fit in the active site properly (see figure below).

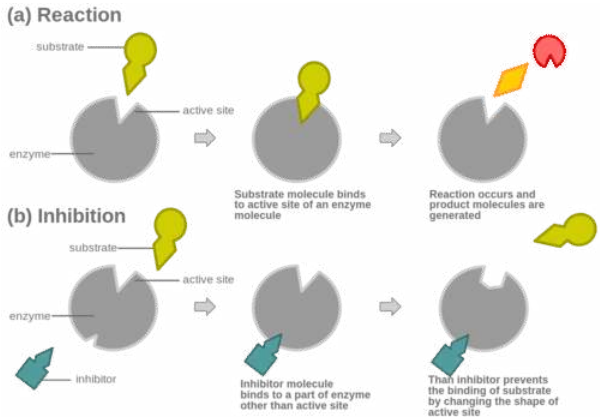


Figure 19.5.13 Non-competitive inhibition.

Cofactors and Coenzymes

Some enzymes require the presence of another substrate as a "helper" molecule in order to function properly. **Cofactors** and **coenzymes** serve in this role. Cofactors are inorganic species and coenzymes are small organic molecules. Many vitamins, such as B vitamins, are coenzymes. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Catalytic Activity of Enzymes

Enzymes generally lower activation energy by reducing the energy needed for reactants to come together and react. One way that enzymes act is to bring reactants (substrates) together so they don't have to expend energy moving about until they collide at random. Enzymes bind both reactant molecules (substrates), tightly and specifically, at a site on the enzyme's active site. Enzymes can also bring molecules to the active site to break them apart. For example, sucrase is the enzyme for the breakdown of sucrose which enters the active site of the enzyme and helps weaken the interactions between the fructose and glucose that make up sucrose. Sucrase is specific to the breakdown of sucrose as are most enzymes. The active site is specific for the reactants of the biochemical reaction the enzyme catalyzes. Similar to puzzle pieces fitting together, the active site can only bind certain substrates. The activities of enzymes also depend on the temperature, concentration, and the pH of the surroudings.

Concentration

As with most reactions, the concentration of the reactant(s) affects the reaction rate. This is also true in enzyme concentration. When either substrate or enzyme concentration is low, the rate of the reaction will be slower than where there are higher concentrations. The two species must interact for a reaction to occur and higher concentrations of one or both will result in more effective interactions between the two.

However, continuing to increase the substrate's concentration will not always increase the reaction rate. This is because at some point, all of the enzymes will be occupied and unavailable to bind with another substrate molecule until the substrate forms a product molecule and is released from the enzyme.

pH

Some enzymes work best at acidic pHs, while others work best in neutral environments. For example, digestive enzymes secreted in the acidic environment (low pH) of the stomach help break down proteins into smaller molecules. The main digestive enzyme in the stomach is **pepsin**, which works best at a pH of about 1.5. These enzymes would not work optimally at other pHs. Trypsin is another enzyme in the digestive system, which breaks protein chains in food into smaller particles. **Trypsin** works in the small intestine, which is not an acidic environment. Trypsin's optimum pH is about 8.

Different reactions and different enzymes will achieve their maximum rate at certain pH values. As shown in the figure below, the enzyme achieves a maximum reaction rate at a pH of 4. Notice that the reaction will continue at lower and higher pH values because the enzyme will still function at other pH values but will not be as effective. At very high or very low pH values, denaturation will occur because an enzyme is just a protein with a specific function.

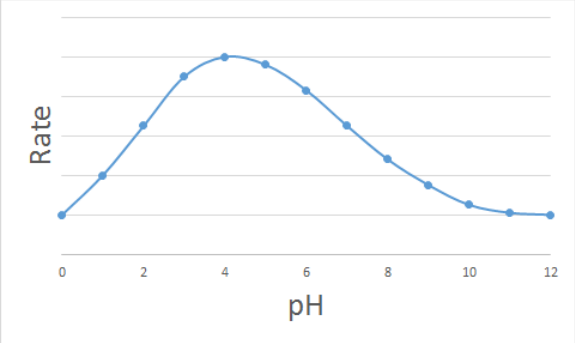


Figure **19.5.14** Relationship between rate and pH.

Temperature

As with pH, reactions also have an ideal temperature where the enzyme functions most effectively. It will still function at higher and lower temperatures, but the rate will be less. For many biological reactions, the ideal temperature is at physiological conditions which is around **37°C** which is normal body temperature. Many enzymes lose function at lower and higher temperatures. At higher temperatures, an enzyme's shape deteriorates. Only when the temperature comes back to normal does the enzyme regain its shape and normal activity unless the temperature was so high that it caused irreversible damage.

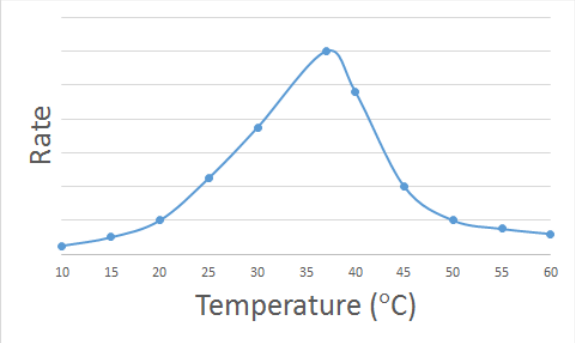


Figure **19.5.15** *Relationship between temperature and rate*.

Applications of Enzymes

Enzymes are used in the and other industrial applications when extremely specific catalysts are required (Table **19.5.1**). Enzymes in general are limited in the number of reactions they have evolved to catalyze and also by their lack of stability in and at high temperatures. As a consequence, is an active area of research and involves attempts to create new enzymes with novel properties, either through rational design or *in vitro* evolution. These efforts have begun to be successful, and a few enzymes have now been designed "from scratch" to catalyze reactions that do not occur in nature.

Table **19.5.1** *Uses of Enzymes in Various Industries. Source: Wikipedia*

Application	Enzymes used	Uses
Biofuel industry	Cellulases	Break down cellulose into sugars that can be fermented to produce cellulosic ethanol.
	Ligninases	Pretreatment of biomass for biofuel production.
Biological detergent	Proteases, amylases, lipases	Remove protein, starch, and fat or oil stains from laundry and dish ware.
	Mannanases	Remove food stains from the common food additive guar gum.
Brewing industry	Amylase, glucanases, proteases	Split polysaccharides and proteins in the malt.
	Betaglucanases	Improve the wort and beer filtration characteristics.
	Amyloglucosisdase and pullulanases	Make low-calorie beer and adjust fermentability.
	Acetolacatate deacrboxylase (ALDC)	Increase fermentation efficiency by reducing diacetyl formation.
Culinary uses	Papain	Tenderize meat for cooking.
Dairy industry	Renin	Hydrolyze protein in the manufacture of cheese.
	Lipases	Produce Camembert cheese and blue cheese such as Roquefort.
Food processing	Amylases	Produce sugars from starch, such as in making high-fructose corn syrup.
	Proteases	Lower the protein level of flour, as in biscuit-making.
	Trypsin	Manufacture hypoallergenic baby foods.
	Cellulases, pectinases	Clarify fruit juices.
Molecular biology	Nucleases, DNA ligase, and polymerases	Use restriction digestion and the polymerase chain reaction to create recombinant DNA.
Paper industry	Xylanases, hemicellulases, and lignin peroxidases	Remove lignin from Kraft pulp.
Personal care	Proteases	Remove proteins on cotact lenses to prevent infections.
Starch industry	Amylases	Convert starch into glucose and various syrups.



https://www.youtube.com/watch?v=E90D4BmaVJM

Summary

- Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure.
- The primary structure consists of the specific amino acid sequence.
- The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain.
- The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces.
- An enzyme is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature.
- The molecule or molecules on which an enzyme acts are called its substrates.
- An enzyme has an active site where its substrate or substrates bind to form an enzyme-substrate complex.
- The original lock and key model of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer induced fit model describes the enzyme active site as changing its conformation after binding to the substrate.
- Enzymes have numerous applications in the food and dairy industry, biofuel industry, paper industry etc.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)
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19.6: Membranes and Membrane Lipids

Learning Objectives

- Identify the distinguishing characteristics of membrane lipids.
- Describe membrane components and how they are arranged.

All living cells are surrounded by a cell membrane. Plant cells (Figure **19.6.1*A***) and animal cells (Figure **19.6.1*B***) contain a cell nucleus that is also surrounded by a membrane and holds the genetic information for the cell. Everything between the cell membrane and the nuclear membrane—including intracellular fluids and various subcellular components such as the mitochondria and ribosomes—is called the cytoplasm. The membranes of all cells have a fundamentally similar structure, but membrane function varies tremendously from one organism to another and even from one cell to another within a single organism. This diversity arises mainly from the presence of different proteins and lipids in the membrane.

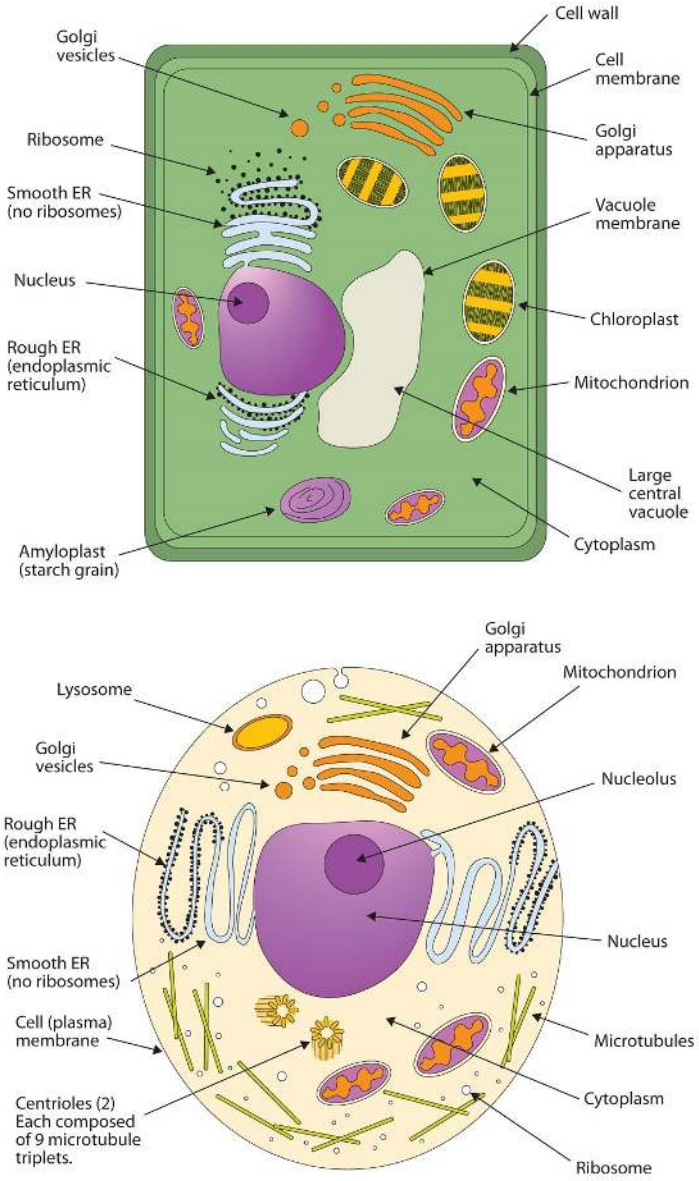


Figure **19.6.1**: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

The lipids in cell membranes are highly polar but have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. Often, the ionic part is referred to as hydrophilic, meaning “water loving,” and the nonpolar part as hydrophobic, meaning “water fearing” (repelled by water). When allowed to float freely in water, polar lipids spontaneously cluster together in any one of three arrangements: micelles, monolayers, and bilayers (Figure **19.6.2**).

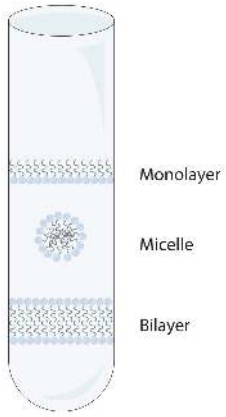


Figure **19.6.2**: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

Micelles are aggregations in which the lipids’ hydrocarbon tails—being hydrophobic—are directed toward the center of the assemblage and away from the surrounding water while the hydrophilic heads are directed outward, in contact with the water. Each micelle may contain thousands of lipid molecules. Polar lipids may also form a monolayer, a layer one molecule thick on the surface of the water. The polar heads face into water, and the nonpolar tails stick up into the air. Bilayers are double layers of lipids arranged so that the hydrophobic tails are sandwiched between an inner surface and an outer surface consisting of hydrophilic heads. The hydrophilic heads are in contact with water on either side of the bilayer, whereas the tails, sequestered inside the bilayer, are prevented from having contact with the water. Bilayers like this make up every cell membrane (Figure **19.6.3**).

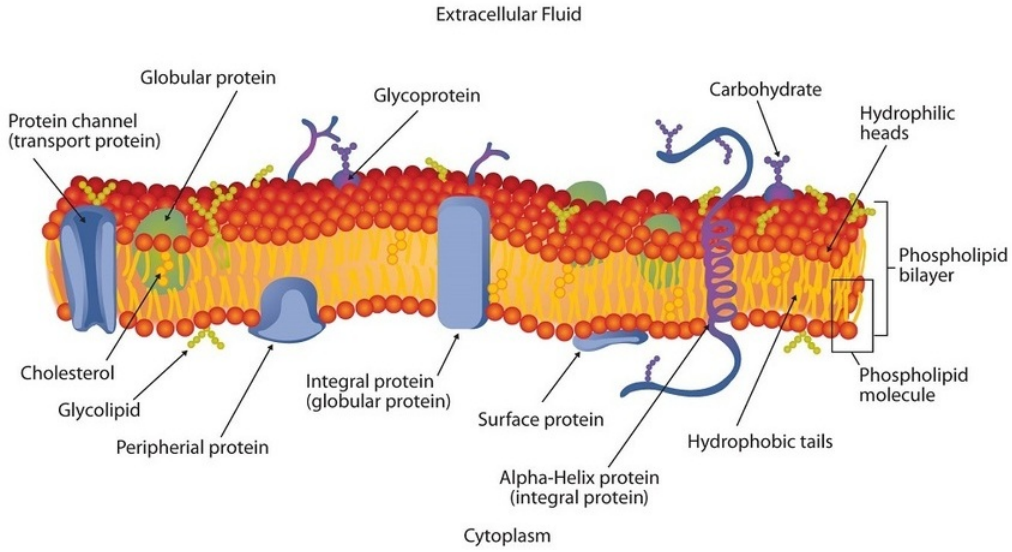


Figure **19.6.3**: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of dispersion forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to mill about to some extent, and the membrane is described as fluid.

The lipids found in cell membranes can be categorized in various ways. Phospholipids are lipids containing phosphorus. Glycolipids are sugar-containing lipids. The latter are found exclusively on the outer surface of the cell membrane, acting as distinguishing surface markers for the cell and thus serving in cellular recognition and cell-to-cell communication. Sphingolipids

are phospholipids or glycolipids that contain the unsaturated amino alcohol sphingosine rather than glycerol. Diagrammatic structures of representative membrane lipids are presented in Figure **19.6.4**.

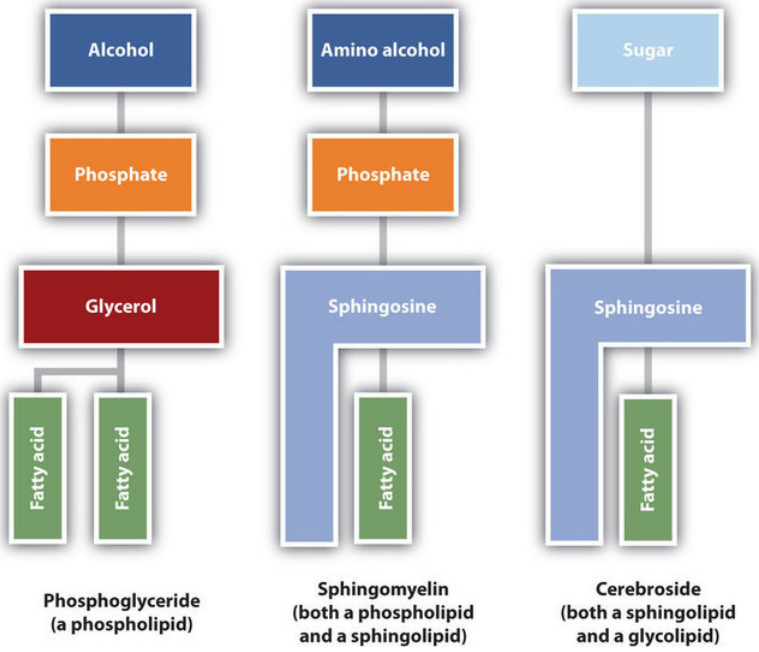


Figure **19.6.4**: Component Structures of Some Important Membrane Lipids

Phosphoglyceride are composed of alcohol, phosphate, glycerol and 2 fatty acids. A sphingomyelin contains phosphate, sphingosine, and a fatty acid. A cerbroside contains sugar, sphingosine and a fatty acid.

Phosphoglycerides (also known as glycerophospholipids) are the most abundant phospholipids in cell membranes. They consist of a glycerol unit with fatty acids attached to the first two carbon atoms, while a phosphoric acid unit, esterified with an alcohol molecule (usually an amino alcohol, as in part (a) of Figure **19.6.5**) is attached to the third carbon atom of glycerol (part (b) of Figure **19.6.5**). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure **19.6.5**).

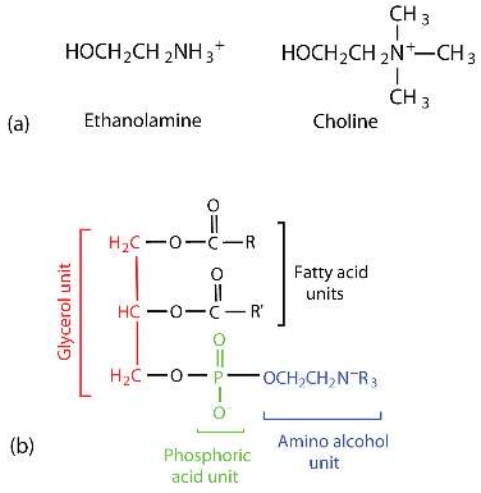
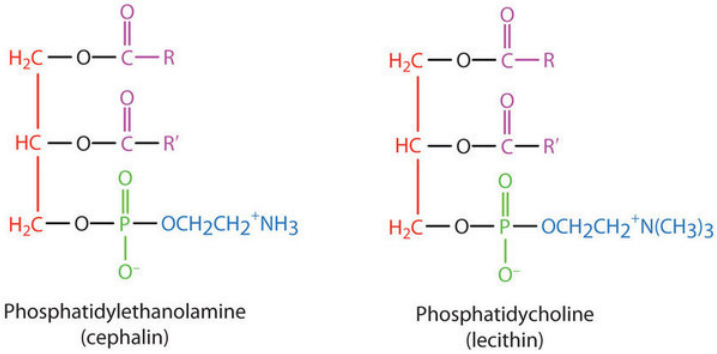


Figure **19.6.5**: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

Structural formula of ethanolamine and choline are shown. The structural formula of a phosphoglyceride is shown with the glycerol unit, phosphoric unit, and amino alcohol unit highlighted in different colors.

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all

living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.



Sphingomyelins, the simplest sphingolipids, each contain a fatty acid, a phosphoric acid, sphingosine, and choline (Figure **19.6.6**). Because they contain phosphoric acid, they are also classified as phospholipids. Sphingomyelins are important constituents of the myelin sheath surrounding the axon of a nerve cell. Multiple sclerosis is one of several diseases resulting from damage to the myelin sheath.

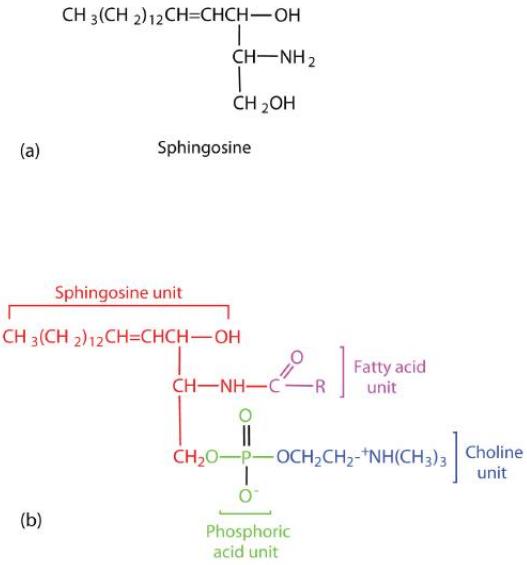


Figure **19.6.6**: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

Structural formula of sphingosine is shown. The general structure of a sphingolipid is shown with the sphingosine unit, fatty acid unit, phosphoric acid unit, and choline unit highlighted in different colors.

Most animal cells contain sphingolipids called cerebrosides (Figure **19.6.7**). Cerebrosides are composed of sphingosine, a fatty acid, and galactose or glucose. They therefore resemble sphingomyelins but have a sugar unit in place of the choline phosphate group. Cerebrosides are important constituents of the membranes of nerve and brain cells.

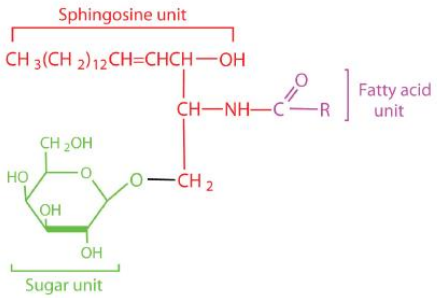


Figure 19.6.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

The sphingolipids called gangliosides are more complex, usually containing a branched chain of three to eight monosaccharides and/or substituted sugars. Because of considerable variation in their sugar components, about 130 varieties of gangliosides have been identified. Most cell-to-cell recognition and communication processes (e.g., blood group antigens) depend on differences in the sequences of sugars in these compounds. Gangliosides are most prevalent in the outer membranes of nerve cells, although they also occur in smaller quantities in the outer membranes of most other cells. Because cerebrosides and gangliosides contain sugar groups, they are also classified as glycolipids.

Membrane Proteins

If membranes were composed only of lipids, very few ions or polar molecules could pass through their hydrophobic "sandwich filling" to enter or leave any cell. However, certain charged and polar species do cross the membrane, aided by proteins that move about in the lipid bilayer. The two major classes of proteins in the cell membrane are integral proteins, which span the hydrophobic interior of the bilayer, and peripheral proteins, which are more loosely associated with the surface of the lipid bilayer (Figure **19.6.3**). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

Small ions and molecules soluble in water enter and leave the cell by way of channels through the integral proteins. Some proteins, called *carrier proteins*, facilitate the passage of certain molecules, such as hormones and neurotransmitters, by specific interactions between the protein and the molecule being transported.

Summary

Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

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19.7: Nucleotides

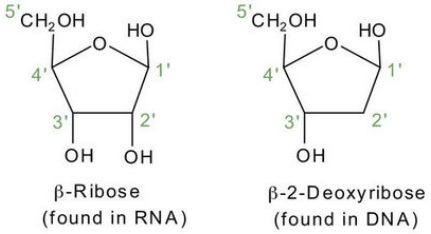
Learning Objectives

- 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 **19.7.1**).

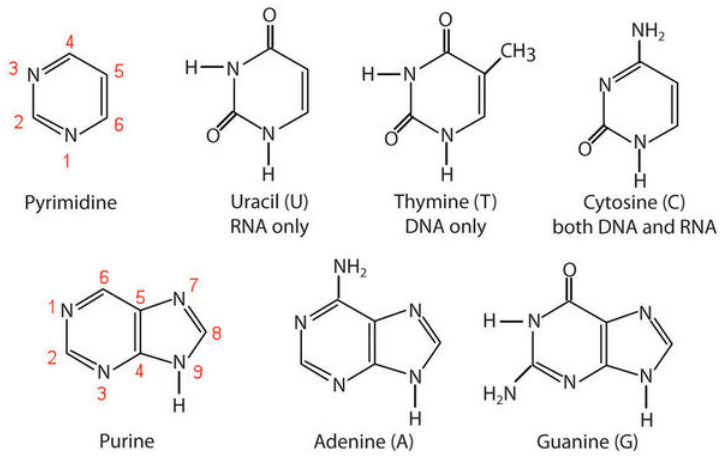


Figure **19.7.1**: The Nitrogenous Bases Found in DNA and RNA

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 **19.7.1** 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 **19.7.1**: 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 **19.7.2**.

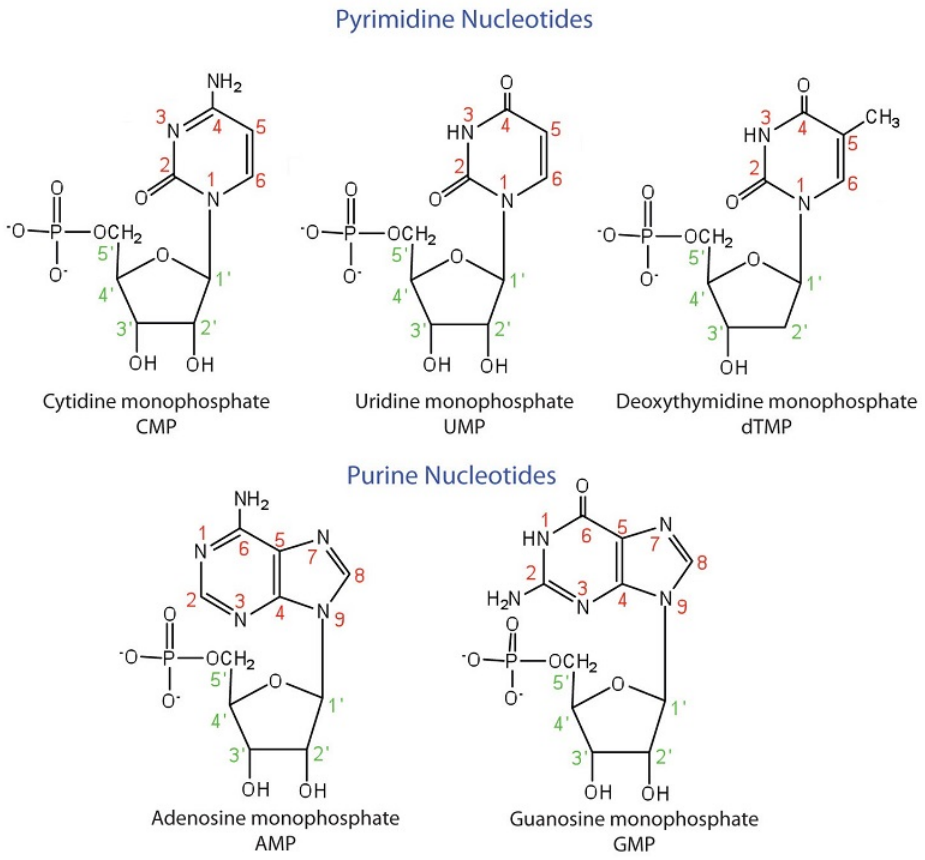


Figure **19.7.2**: The Pyrimidine and Purine Nucleotides

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 **19.7.3**, 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.

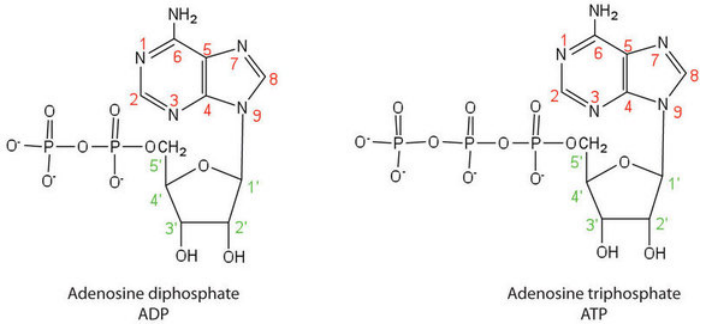


Figure **19.7.3**: Structures of Two Important Adenine-Containing Nucleotides

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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19.8: Nucleic Acids- Parts, Structure, and Function

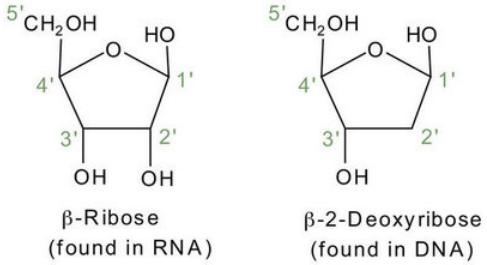
Learning Objectives

- Describe the two types of nucleic acids and the function of each type.
- Describe the secondary structure of DNA and the importance of complementary base pairing.
- Describe how a new copy of DNA is synthesized.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure **19.8.1**).

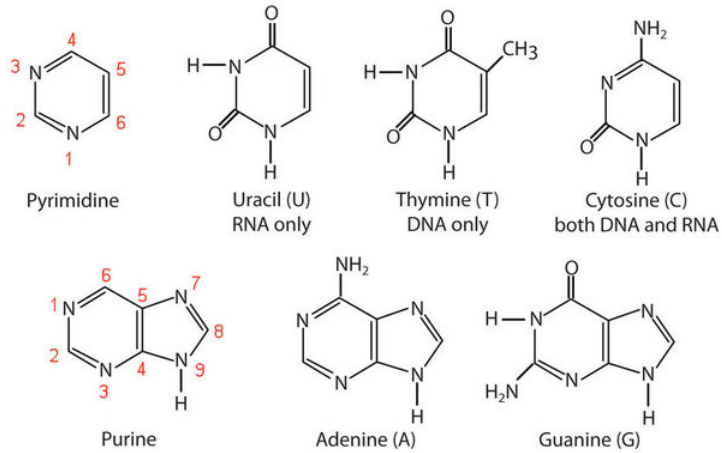


Figure **19.8.1** The Nntrogenous bases found in DNA and RNA.

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table **19.8.1** 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 19.8.1 Composition of Nucleotides in DNA and RNA.

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
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pentose sugar	2-deoxyribose	ribose
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The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure 19.8.2.

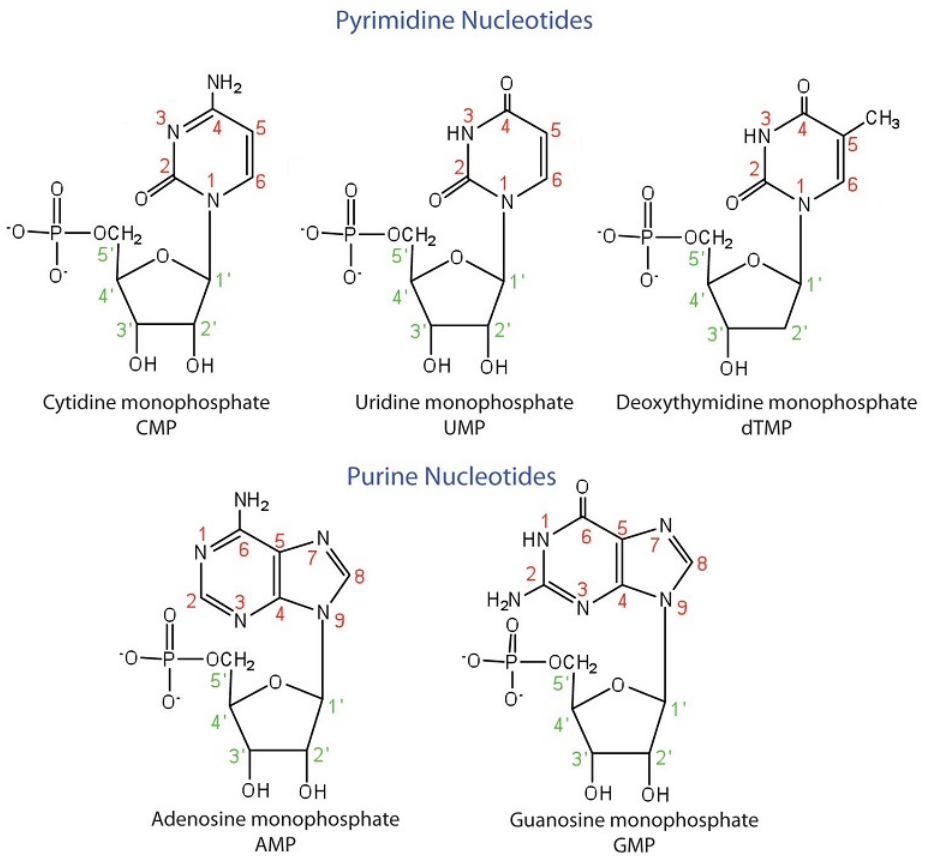


Figure 19.8.2 The pyrimidine and purine nucleotides

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 19.8.3, 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.

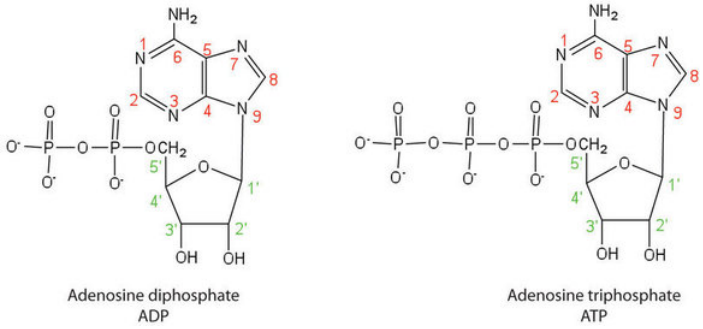


Figure **19.8.3** *Structures of two important adenine-containing nucleotides.*

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure **19.8.4**). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

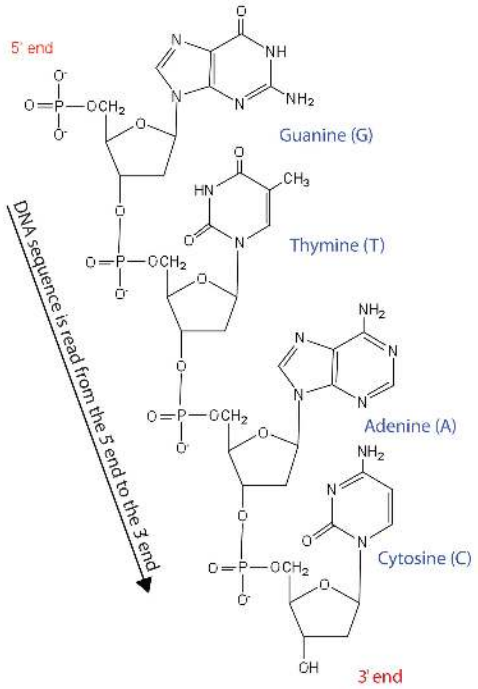


Figure **19.8.4** Structure of a segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases,

shown in Figure 19.8.4) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 19.8.4 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 19.8.5).

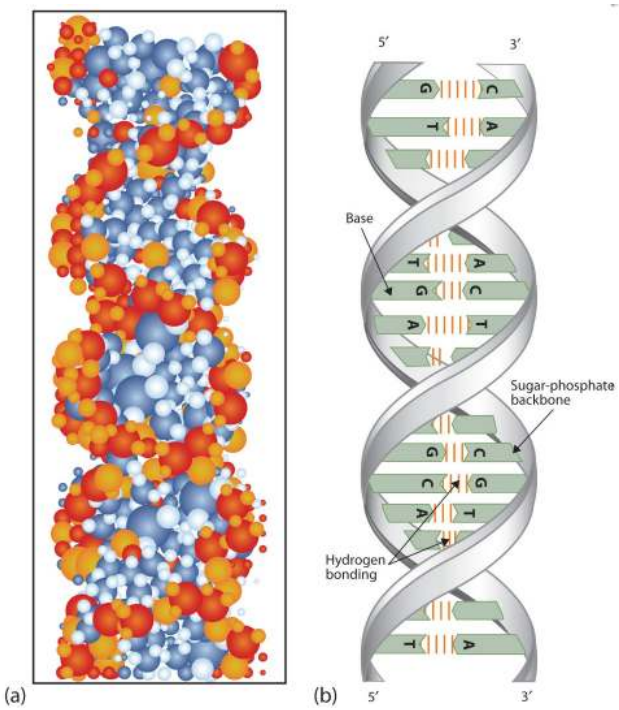


Figure 19.8.5 DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 19.8.6 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

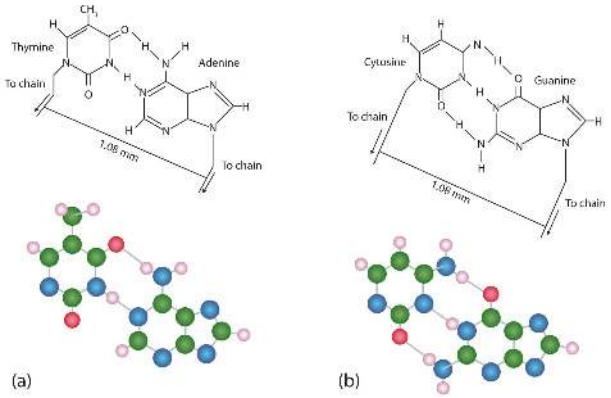


Figure **19.8.6** Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure **19.8.7**. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure **19.8.6** is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

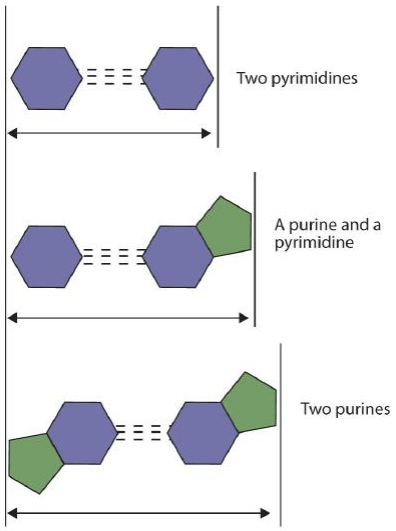


Figure **19.8.7** Difference in Widths of Possible Base Pairs

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

DNA: Self-Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is “unzipped,” so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme,

recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure 19.8.8). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

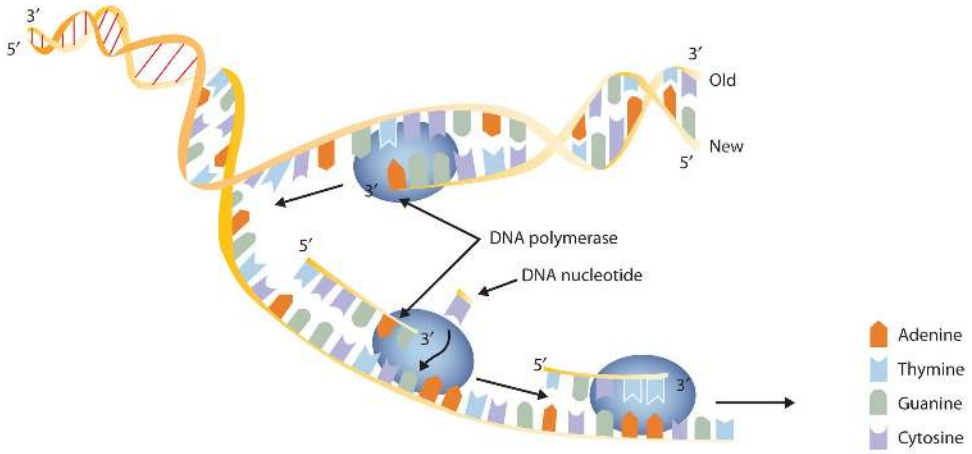


Figure 19.8.8 A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

✔ Example 19.8.1

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′.

? Exercise 19.8.1

A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Answer

3′-GGTCACTTAACGGATA-5′.

Summary

- Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.
- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.
- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.

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19.9: RNA Protein Synthesis and the Genetic Code

Learning Objectives

- Describe the characteristics of the genetic code.
- Describe how a protein is synthesized from mRNA.

One of the definitions of a gene is as follows: a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are 4^2, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is 4^3, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.



***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see http://vcell.ndsu.nodak.edu/animations*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

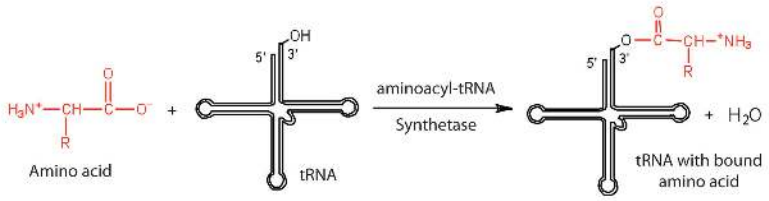
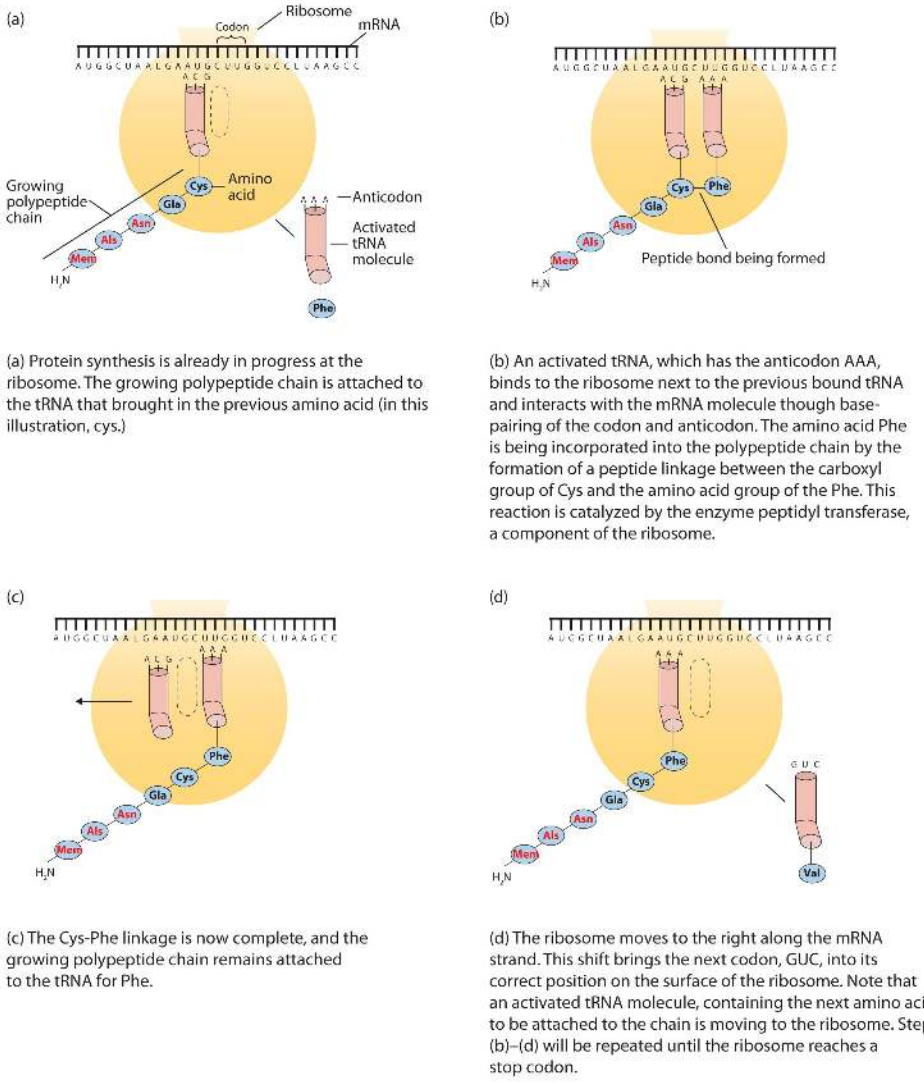


Figure 19.9.1: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure 19.9.1). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. Figure 19.9.2 depicts a schematic stepwise representation of this all-important process.



(a) Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

(b) An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though base-pairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide chain by the formation of a peptide linkage between the carboxyl group of Cys and the amino acid group of the Phe. This reaction is catalyzed by the enzyme peptidyl transferase, a component of the ribosome.

(c) The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

(d) The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)–(d) will be repeated until the ribosome reaches a stop codon.

Figure 19.9.2: The Elongation Steps in Protein Synthesis

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 19.9.3, shows that 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much

like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.

First base	Second base: U	Second base: C	Second base: A	Second base: G	Third base
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Stop	Stop	A
	Leu	Ser	Stop	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

Figure **19.9.3**: The Genetic Code

Example 19.9.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

Solution

Use Figure **19.9.3** to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid. The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

Exercise 19.9.1

A portion of an mRNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

met-leu-asn-cys-val-gly

The Nature of the Genetic Code

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan), more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.
5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.

6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

Summary

- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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19.10: Viruses

Learning Objectives

- To explain how viruses reproduce in cells.

Viruses are visible only under an electron microscope. They come in a variety of shapes, ranging from spherical to rod shaped. The fact that they contain either deoxyribonucleic acid (DNA) or ribonucleic acid (RNA)—*but never both*—allows them to be divided into two major classes: DNA viruses and RNA viruses (Figure **19.10.1**).

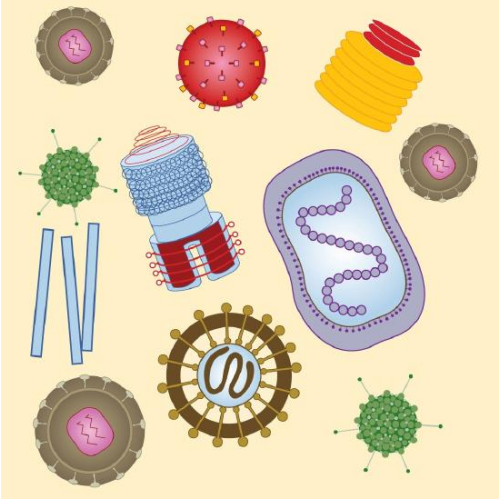


Figure **19.10.1**: Viruses. Viruses come in a variety of shapes that are determined by their protein coats.

Most *RNA viruses* use their nucleic acids in much the same way as the DNA viruses, penetrating a host cell and inducing it to replicate the viral RNA and synthesize viral proteins. The new RNA strands and viral proteins are then assembled into new viruses. Some RNA viruses, however, called retroviruses (Figure **19.10.2**), synthesize DNA in the host cell, in a process that is the reverse of the DNA-to-RNA transcription that normally occurs in cells. The synthesis of DNA from an RNA template is catalyzed by the enzyme reverse transcriptase.

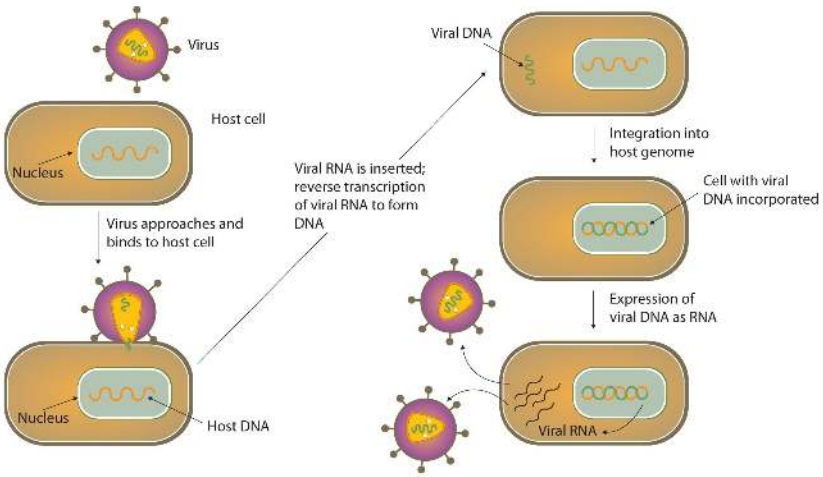
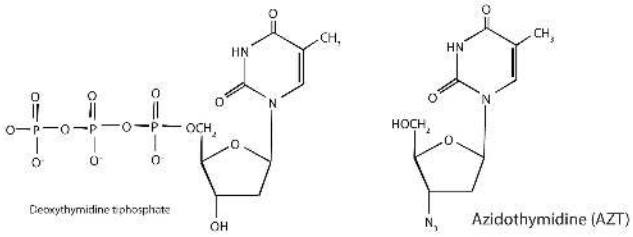
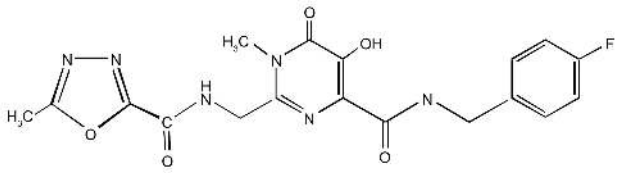


Figure **19.10.2**: Life Cycle of a Retrovirus

In 1987, **azidothymidine** (AZT, also known as zidovudine or the brand name Retrovir) became the first drug approved for the treatment of AIDS. It works by binding to reverse transcriptase in place of deoxythymidine triphosphate, after which, because AZT does not have a 3′OH group, further replication is blocked. In the past 10 years, several other drugs have been approved that also act by inhibiting the viral reverse transcriptase.



Raltegravir (Isentress) is a newer anti-AIDS drug that was approved by the FDA in October 2007. This drug inhibits the integrase enzyme that is needed to integrate the HIV DNA into cellular DNA, an essential step in the production of more HIV particles.



A major problem in treating HIV infections is that the virus can become resistant to any of these drugs. One way to combat the problem has been to administer a “cocktail” of drugs, typically a combination of two reverse transcriptase inhibitors along with a protease inhibitor. These treatments can significantly reduce the amount of HIV in an infected person.

Career Focus: Genetics Counselor

A genetics counselor works with individuals and families who have birth defects or genetic disorders or a family history of a disease, such as cancer, with a genetic link. A genetics counselor may work in a variety of health-care settings (such as a hospital) to obtain family medical and reproductive histories; explain how genetic conditions are inherited; explain the causes, diagnosis, and care of these conditions; interpret the results of genetic tests; and aid the individual or family in making decisions regarding genetic diseases or conditions. A certified genetics counselor must obtain a master’s degree from an accredited program. Applicants to these graduate programs usually have an undergraduate degree in biology, psychology, or genetics.



Photo courtesy of the United States National Institutes for Health, commons.wikimedia.org/wiki/File:Geneticcounseling.jpg.

Summary

Viruses are very small infectious agents that contain either DNA or RNA as their genetic material. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

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19.E: Nucleic Acids (Exercises)

19.1: Nucleotides

Concept Review Exercises

1. Identify the three molecules needed to form the nucleotides in each nucleic acid.
   a. DNA
   b. RNA
2. Classify each compound as a pentose sugar, a purine, or a pyrimidine.
   a. adenine
   b. guanine
   c. deoxyribose
   d. thymine
   e. ribose
   f. cytosine

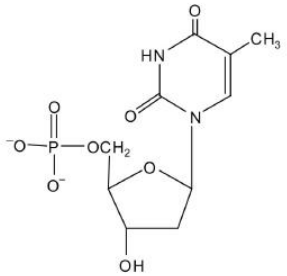
Answers

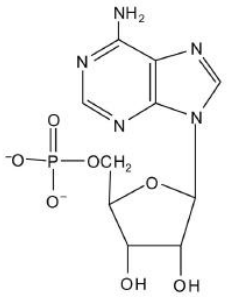
1. a. nitrogenous base (adenine, guanine, cytosine, and thymine), 2-deoxyribose, and H_3PO_4
   b. nitrogenous base (adenine, guanine, cytosine, and uracil), ribose, and H_3PO_4
2. a. purine
   b. purine
   c. pentose sugar
   d. pyrimidine
   e. pentose sugar
   f. pyrimidine

Exercises

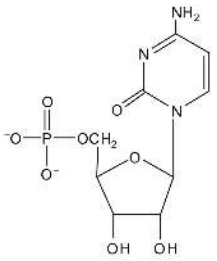
1. What is the sugar unit in each nucleic acid?
   a. RNA
   b. DNA
2. Identify the major nitrogenous bases in each nucleic acid.
   a. DNA
   b. RNA
3. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

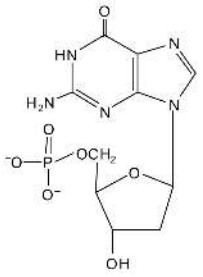
   a.



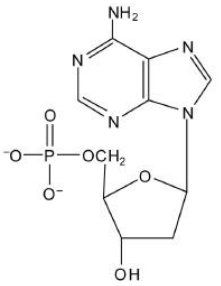
b. 

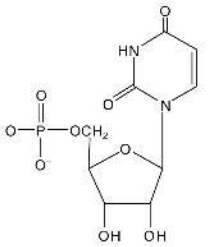
4. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a. 

b. 

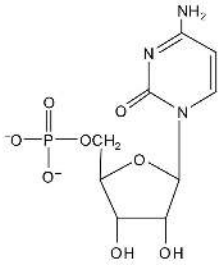
5. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a. 

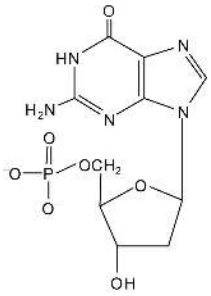
b. 

6. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.



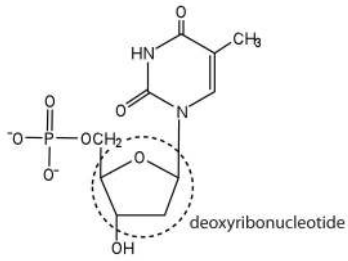
b.



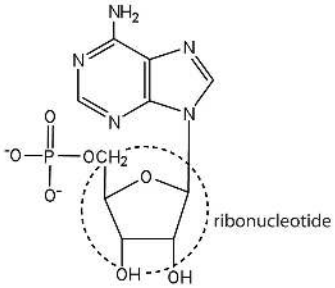
Answers

1. a. ribose
   b. deoxyribose

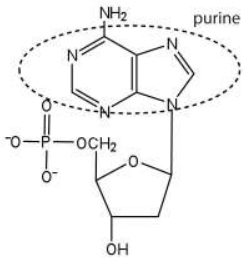
3. a.



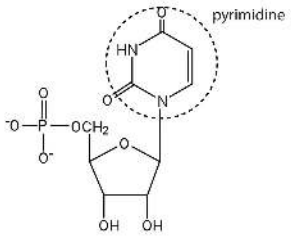
b.



a.



b.



19.2: Nucleic Acid Structure

Concept Review Exercises

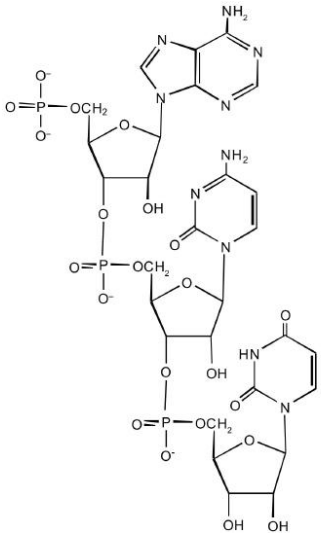
1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

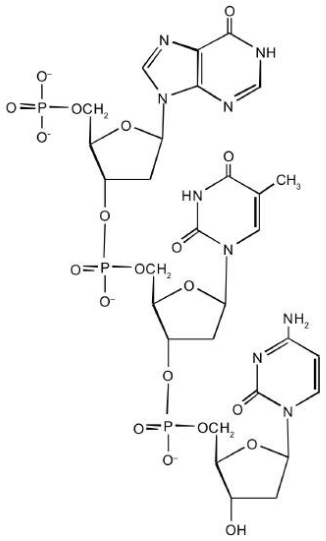
1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines 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.

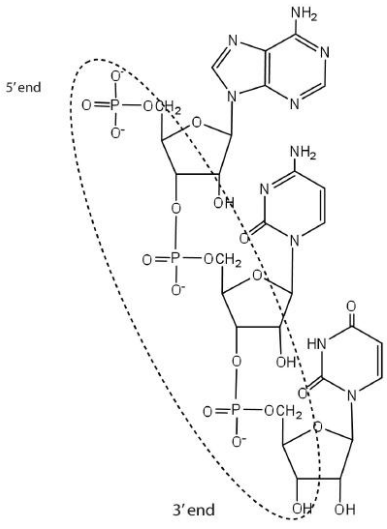


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
5. How many hydrogen bonds can form between the 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)

19.3: Replication and Expression of Genetic Information

Concept Review Exercises

1. In DNA replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
2. What is the role of DNA in transcription? What is produced in transcription?
3. Which type of RNA contains the codon? Which type of RNA contains the anticodon?

Answers

1. Each strand of the parent DNA double helix remains associated with the newly synthesized DNA strand.
2. DNA serves as a template for the synthesis of an RNA strand (the product of transcription).
3. codon: mRNA; anticodon: tRNA

Exercises

1. Describe how replication and transcription are similar.
2. Describe how replication and transcription differ.
3. A portion of the coding strand for a given gene has the sequence 5′-ATGAGCGACTTTGCGGGATTA-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?
4. A portion of the coding strand for a given gene has the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Answers

1. Both processes require a template from which a complementary strand is synthesized.

3.

a. 3′-TACTCGCTGAAACGCCCTAAT-5′
b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

19.4: Protein Synthesis and the Genetic Code

Concept Review Exercises

1. What are the roles of mRNA and tRNA in protein synthesis?
2. What is the initiation codon?
3. What are the termination codons and how are they recognized?

Answers

1. mRNA provides the code that determines the order of amino acids in the protein; tRNA transports the amino acids to the ribosome to incorporate into the growing protein chain.
2. AUG
3. UAA, UAG, and UGA; they are recognized by special proteins called release factors, which signal the end of the translation process.

Exercises

1. Write the anticodon on tRNA that would pair with each mRNA codon.
   a. 5′-UUU-3′
   b. 5′-CAU-3′
   c. 5′-AGC-3′
   d. 5′-CCG-3′
2. Write the codon on mRNA that would pair with each tRNA anticodon.
   a. 5′-UUG-3′
   b. 5′-GAA-3′
   c. 5′-UCC-3′
   d. 5′-CAC-3′
3. The peptide hormone oxytocin contains 9 amino acid units. What is the minimum number of nucleotides needed to code for this peptide?
4. Myoglobin, a protein that stores oxygen in muscle cells, has been purified from a number of organisms. The protein from a sperm whale is composed of 153 amino acid units. What is the minimum number of nucleotides that must be present in the mRNA that codes for this protein?
5. Use Figure **19.*E*.3** to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure **19.*E*.3** to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure **19.*E*.3** to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure **19.*E*.3** to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGGCAAUCCUCAAACGCUGU-3′

Answers

1. a. 3′-AAA-5′
   b. 3′-GUA-5′
   c. 3′-UCG-5′
   d. 3′-GGC-5′
3. 27 nucleotides (3 nucleotides/codon)
5. 1a: phenyalanine; 1b: histidine; 1c: serine; 1d: proline
7. met-ser-asp-phe-ala-gly-leu

19.5: Mutations and Genetic Diseases

Concept Review Exercises

1. a. What effect can UV radiation have on DNA?
   b. Is UV radiation an example of a physical mutagen or a chemical mutagen?
2. a. What causes PKU?
   b. How is PKU detected and treated?

Answers

1. a. It can lead to the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer.
   b. physical mutagen
2. a. the absence of the enzyme phenylalanine hydroxylase
   b. PKU is diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites; treatment calls for an individual to be placed on a diet containing little or no phenylalanine.

Exercises

1. A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGAGCGACCTTCGCCCATTA-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
2. A portion of the coding strand of a gene was found to have the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′. A mutation occurred in the gene, making the sequence 5′-ATGGCAATCCTCAACGCTGT-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
3. a. What is a mutagen?
   b. Give two examples of mutagens.
4. For each genetic disease, indicate which enzyme is lacking or defective and the characteristic symptoms of the disease.
   a. PKU
   b. Tay-Sachs disease

Answers

1. a. substitution
   b. Phenylalanine (UUU) would be replaced with leucine (CUU).
3. a. a chemical or physical agent that can cause a mutation
   b. UV radiation and gamma radiation (answers will vary)

19.6: Viruses

Questions

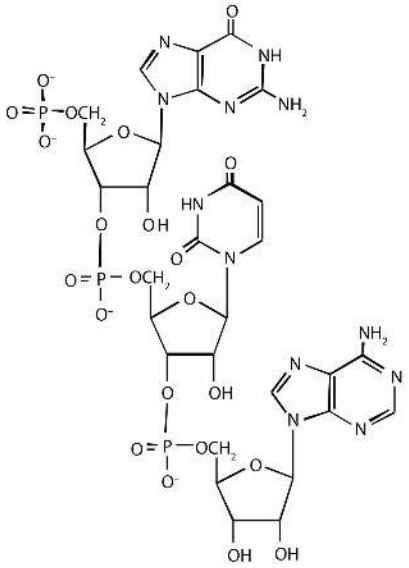
1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5. a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. What HIV enzyme does AZT inhibit?
7. What HIV enzyme does raltegravir inhibit?

Answers

1. A virus consists of a central core of nucleic acid enclosed in a protective shell of proteins. There may be lipid or carbohydrate molecules on the surface.
2. A DNA virus has DNA as its genetic material, while an RNA virus has RNA as its genetic material.
3. In a cell, a retrovirus synthesizes a DNA copy of its RNA genetic material.
4. The DNA virus enters a host cell and induces the cell to replicate the viral DNA and produce viral proteins. These proteins and DNA assemble into new viruses that are released by the host cell, which may die in the process.
5. -
6. reverse transcriptase
7. -

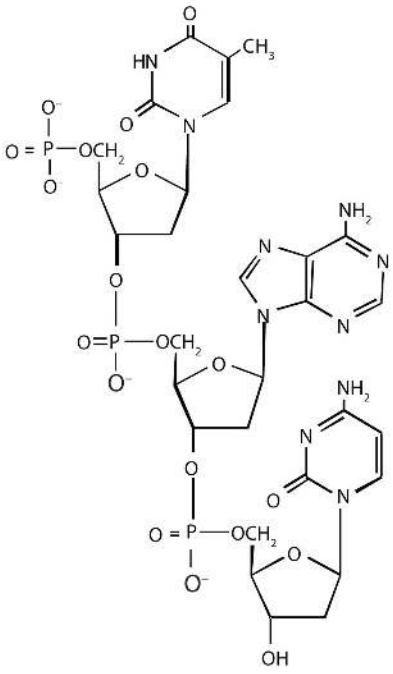
Additional Exercises

1. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

2. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

3. One of the key pieces of information that Watson and Crick used in determining the secondary structure of DNA came from experiments done by E. Chargaff, in which he studied the nucleotide composition of DNA from many different species. Chargaff noted that the molar quantity of A was always approximately equal to the molar quantity of T, and the molar quantity of C was always approximately equal to the molar quantity of G. How were Chargaff's results explained by the structural model of DNA proposed by Watson and Crick?

4. Suppose Chargaff (see Exercise 3) had used RNA instead of DNA. Would his results have been the same; that is, would the molar quantity of A approximately equal the molar quantity of T? Explain.
5. In the DNA segment

   5′-ATGAGGCATGAGACG-3′ (coding strand) 3′-TACTCCGTACTCTGC-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 5b?
6. In the DNA segment

   5′-ATGACGGTTTACTAAGCC-3′ (coding strand) 3′-TACTGCCAAATGATTCGG-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 6b?
7. A hypothetical protein has a molar mass of 23,300 Da. Assume that the average molar mass of an amino acid is 120.

   a. How many amino acids are present in this hypothetical protein?
   b. What is the minimum number of codons present in the mRNA that codes for this protein?
   c. What is the minimum number of nucleotides needed to code for this protein?
8. Bradykinin is a potent peptide hormone composed of nine amino acids that lowers blood pressure.

   a. The amino acid sequence for bradykinin is arg-pro-pro-gly-phe-ser-pro-phe-arg. Postulate a base sequence in the mRNA that would direct the synthesis of this hormone. Include an initiation codon and a termination codon.
   b. What is the nucleotide sequence of the DNA that codes for this mRNA?
9. A particular DNA coding segment is ACGTTAGCCCCAGCT.

   a. Write the sequence of nucleotides in the corresponding mRNA.
   b. Determine the amino acid sequence formed from the mRNA in Exercise 9a during translation.
   c. What amino acid sequence results from each of the following mutations?

      a. replacement of the underlined guanine by adenine
      b. insertion of thymine immediately after the underlined guanine
      c. deletion of the underlined guanine
10. A particular DNA coding segment is TACGACGTAACAAGC.

    a. Write the sequence of nucleotides in the corresponding mRNA.
    b. Determine the amino acid sequence formed from the mRNA in Exercise 10a during translation.
    c. What amino acid sequence results from each of the following mutations?

       a. replacement of the underlined guanine by adenine
       b. replacement of the underlined adenine by thymine
11. Two possible point mutations are the substitution of lysine for leucine *or* the substitution of serine for threonine. Which is likely to be more serious and why?
12. Two possible point mutations are the substitution of valine for leucine *or* the substitution of glutamic acid for histidine. Which is likely to be more serious and why?

Answers

1.

   a. RNA; the sugar is ribose, rather than deoxyribose
   b. 5′-GUA-3′

3. In the DNA structure, because guanine (G) is always paired with cytosine (C) and adenine (A) is always paired with thymine (T), you would expect to have equal amounts of each.

5.

a. Each strand would be replicated, resulting in two double-stranded segments.
b. 5′-AUGAGGCAUGAGACG-3′
c. met-arg-his-glu-thr

7.

a. 194
b. 194
c. 582

9.

a. 5′-ACGUUAGCCCCAGCU-3′
b. thr-leu-ala-pro-ala
c. a. thr-leu-thr-pro-ala
b. thr-leu-val-pro-ser
c. thr-leu-pro-gin

11. substitution of lysine for leucine because you are changing from an amino acid with a nonpolar side chain to one that has a positively charged side chain; both serine and threonine, on the other hand, have polar side chains containing the OH group.

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19.S: Amino Acids, Proteins, and Enzymes (Summary)

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

A **protein** is a large biological polymer synthesized from **amino acids**, which are carboxylic acids containing an α-amino group. Proteins have a variety of important roles in living organisms, yet they are made from the same 20 L-amino acids. About half of these amino acids, the **essential amino acids**, cannot be synthesized by the human body and must be obtained from the diet. In the solid state and in neutral solutions, amino acids exist as **zwitterions**, species that are charged but electrically neutral. In this form, they behave much like inorganic salts. Each amino acid belongs to one of four classes depending on the characteristics of its R group or amino acid side chain: nonpolar, polar but neutral, positively charged, and negatively charged. Depending on the conditions, amino acids can act as either acids or bases, which means that proteins act as buffers. The pH at which an amino acid exists as the zwitterion is called the **isoelectric point (pI)**.

The amino acids in a protein are linked together by **peptide bonds**. Protein chains containing 10 or fewer amino acids are usually referred to as **peptides**, with a prefix such as di- or tri- indicating the number of amino acids. Chains containing more than 50 amino acid units are referred to as *proteins* or **polypeptides**. Proteins are classified globular or fibrous, depending on their structure and resulting solubility in water. **Globular proteins** are nearly spherical and are soluble in water; **fibrous proteins** have elongated or fibrous structures and are not soluble in water.

Protein molecules can have as many as four levels of structure. The **primary structure** is the sequence of amino acids in the chain. The **secondary structure** is the arrangement of adjacent atoms in the peptide chain; the most common arrangements are α-helices or β-pleated sheets. The **tertiary structure** is the overall three-dimensional shape of the molecule that results from the way the chain bends and folds in on itself. Proteins that consist of more than one chain have **quaternary structure**, which is the way the multiple chains are packed together.

Four types of intramolecular and intermolecular forces contribute to secondary, tertiary, and quaternary structure: (1) **hydrogen bonding** between an oxygen or a nitrogen atom and a hydrogen atom bound to an oxygen atom or a nitrogen atom, either on the same chain or on a neighboring chain; (2) **ionic bonding** between one positively charged side chain and one negatively charged side chain; (3) **disulfide linkages** between cysteine units; and (4) **dispersion forces** between nonpolar side chains.

Because of their complexity, protein molecules are delicate and easy to disrupt. A *denatured* protein is one whose conformation has been changed, in a process called **denaturation**, so that it can no longer do its physiological job. A variety of conditions, such as heat, ultraviolet radiation, the addition of organic compounds, or changes in pH can denature a protein.

An **enzyme** is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature. Without the help of enzymes, these reactions would require high temperatures and long reaction times.

The molecule or molecules on which an enzyme acts are called its **substrates**. An enzyme has an **active site** where its substrate or substrates bind to form an enzyme-substrate complex. The reaction occurs, and product is released:

$$E + S \rightarrow E\text{–}S \rightarrow E + P$$

The original **lock-and-key model** of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer **induced-fit model** describes the enzyme active site as changing its conformation after binding to the substrate.

Most enzymes have maximal activity in a narrow pH range centered on an **optimum pH**. In this pH range, the enzyme is correctly folded, and catalytic groups in the active site have the correct charge (positive, negative, or neutral). For most enzymes, the optimum pH is between 6 and 8.

Substances that interfere with enzyme function are called inhibitors. An **irreversible inhibitor** inactivates enzymes by forming covalent bonds to the enzyme, while a **reversible inhibitor** inactivates an enzyme by a weaker, noncovalent interaction that is easier to disrupt. A **competitive inhibitor** is a reversible inhibitor that is structurally similar to the substrate and binds to the active site. When the inhibitor is bound, the substrate is blocked from the active site and no reaction occurs. Because the binding of such

an inhibitor is reversible, a high substrate concentration will overcome the inhibition because it increases the likelihood of the substrate binding. A **noncompetitive inhibitor** binds reversibly at a site distinct from the active site. Thus, it can bind to either the enzyme or the enzyme-substrate complex. The inhibitor changes the conformation of the active site so that the enzyme cannot function properly. Noncompetitive inhibitors are important in **feedback inhibition**, in which the amount of product produced by a series of reactions is carefully controlled. The final product in a series of reactions acts as a noncompetitive inhibitor of the initial enzyme.

Simple enzymes consist entirely of one or more amino acid chains. Complex enzymes are composed of one or more amino acid chains joined to **cofactors**—inorganic ions or organic **coenzymes**. **Vitamins** are organic compounds that are essential in very small amounts for the maintenance of normal metabolism and generally cannot be synthesized at adequate levels by the body. Vitamins are divided into two broad categories: *fat-soluble* vitamins and *water-soluble* vitamins. Many of the water-soluble vitamins are used for the synthesis of coenzymes.

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19.S: Nucleic Acids (Summary)

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

A cell's hereditary information is encoded in **chromosomes** in the cell's nucleus. Each chromosome is composed of proteins and **deoxyribonucleic acid (DNA)**. The chromosomes contain smaller hereditary units called **genes,** which are relatively short segments of DNA. The hereditary information is expressed or used through the synthesis of **ribonucleic acid (RNA)**. Both **nucleic acids**—DNA and RNA—are polymers composed of monomers known as **nucleotides**, which in turn consist of phosphoric acid (H_3PO_4), a nitrogenous base, and a pentose sugar.

The two types of *nitrogenous bases* most important in nucleic acids are **purines**—adenine (A) and guanine (G)—and **pyrimidines**—cytosine (C), thymine (T), and uracil (U). DNA contains the nitrogenous bases adenine, cytosine, guanine, and thymine, while the bases in RNA are adenine, cytosine, guanine, and uracil. The sugar in the nucleotides of RNA is ribose; the one in DNA is 2-deoxyribose. The sequence of nucleotides in a nucleic acid defines the primary structure of the molecule.

RNA is a single-chain nucleic acid, whereas DNA possesses two nucleic-acid chains intertwined in a secondary structure called a **double helix**. The sugar-phosphate backbone forms the outside the double helix, with the purine and pyrimidine bases tucked inside. Hydrogen bonding between **complementary bases** holds the two strands of the double helix together; A always pairs with T and C always pairs with G.

Cell growth requires **replication**, or reproduction of the cell's DNA. The double helix unwinds, and hydrogen bonding between complementary bases breaks so that there are two single strands of DNA, and each strand is a *template* for the synthesis of a new strand. For protein synthesis, three types of RNA are needed: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). All are made from a DNA template by a process called **transcription**. The double helix uncoils, and ribonucleotides base-pair to the deoxyribonucleotides on one DNA strand; however, RNA is produced using *uracil* rather than thymine. Once the RNA is formed, it dissociates from the template and leaves the nucleus, and the DNA double helix reforms.

Translation is the process in which proteins are synthesized from the information in mRNA. It occurs at structures called **ribosomes**, which are located outside the nucleus and are composed of rRNA and protein. The 64 possible three-nucleotide combinations of the 4 nucleotides of DNA constitute the **genetic code** that dictates the sequence in which amino acids are joined to make proteins. Each three-nucleotide sequence on mRNA is a **codon**. Each kind of tRNA molecule binds a specific amino acid and has a site containing a three-nucleotide sequence called an **anticodon**.

The general term for any change in the genetic code in an organism's DNA is **mutation**. A change in which a single base is substituted, inserted, or deleted is a **point mutation**. The chemical and/or physical agents that cause mutations are called **mutagens**. Diseases that occur due to mutations in critical DNA sequences are referred to as **genetic diseases**.

Viruses are infectious agents composed of a tightly packed central core of nucleic acids enclosed by a protective shell of proteins. Viruses contain either DNA or RNA as their genetic material but not both. Some RNA viruses, called **retroviruses**, synthesize DNA in the host cell from their RNA genome. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

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CHAPTER OVERVIEW

20: Appendices

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General Chemistry

20.1: Essential Mathematics

20.2: Units and Conversion Factors

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20.1: Essential Mathematics

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$1000 = 1 \times 10^3$$
$$100 = 1 \times 10^2$$
$$10 = 1 \times 10^1$$
$$1 = 1 \times 10^0$$
$$0.1 = 1 \times 10^{-1}$$
$$0.001 = 1 \times 10^{-3}$$
$$2386 = 2.386 \times 1000 = 2.386 \times 10^3$$
$$0.123 = 1.23 \times 0.1 = 1.23 \times 10^{-1}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, 1,230,000,000 = 1.23×10^9, and 0.00000000036 = 3.6×10^{-10}.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 20.1.1: Adding Exponentials

Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

$$3.00 \times 10^{-3} = 300 \times 10^{-5}$$
$$(5.00 \times 10^{-5}) + (300 \times 10^{-5}) = 305 \times 10^{-5} = 3.05 \times 10^{-3}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 20.1.2: Subtracting Exponentials

Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6}$$
$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Exercise 20.1.3: Multiplying Exponentials

Multiply 4.2×10^{-8} by 2.0×10^3.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Exercise 20.1.4: Dividing Exponentials

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Exercise 20.1.5: Squaring Exponentials

Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2\times(-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Exercise 20.1.6: Cubing Exponentials

Cube the number 2×10^{4}.

Solution

$$(2 \times 10^{4})^3 = 2 \times 2 \times 2 \times 10^{3\times4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Exercise 20.1.7: Finding the Square Root of Exponentials

Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the

computation (indicated by underscoring in the following example).

Exercise 20.1.8: Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

$$\begin{array}{r} 4.38\underline{3}\ \text{g} \\ +\ 0.00\underline{23}\ \text{g} \\ \hline 4.38\underline{5}\ \text{g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Exercise 20.1.9: Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \times 6.\underline{6} = 4.\underline{1}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers. \[\log xy= \log x + \log y, \textrm{ and }\ln xy=\ln x + \ln y \nonumber \]
2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers. \[\log\dfrac{x}{y}=\log x-\log y,\textrm{ and } \ln\dfrac{x}{y}=\ln x-\ln y \nonumber \]
3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solving Quadratic Equations Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x*-*y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

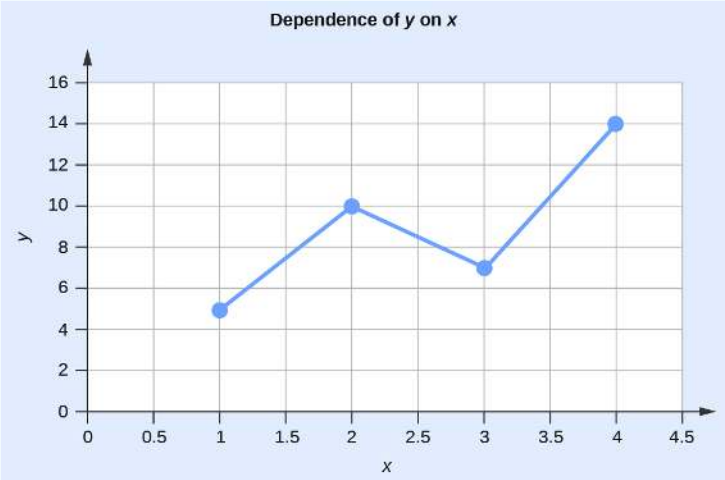
Exercise 20.1.10

Graphing the Dependence of y on x

Table for Exercise 10

x	y
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x.



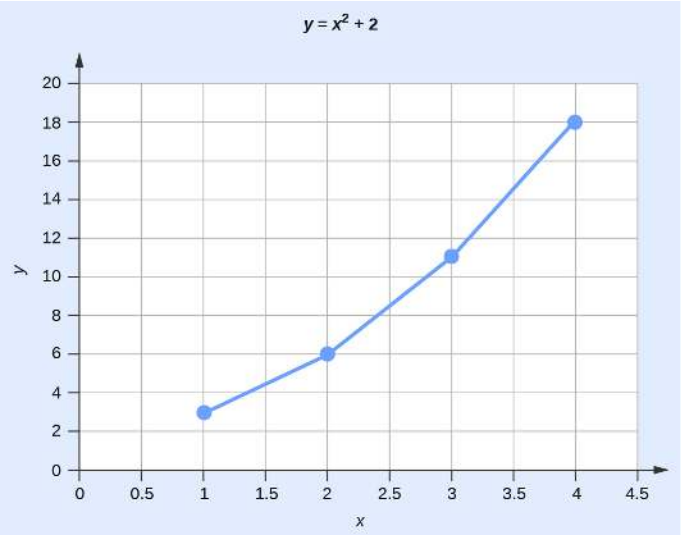
If the function that describes the dependence of y on x is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Exercise 20.1.11

Plotting Data Pairs If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

Table for Exercise 11

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



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20.2: Units and Conversion Factors

Units of Length

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume

Units of Volume			
liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts	liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)	dry quart	= 1.1012 L
microliter (μL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)	cubic foot (US)	= 28.316 L

Units of Mass

Units of Mass			
gram (g)	= 0.001 kg (exact, definition)	ounce (oz) (avoirdupois)	= 28.35 g
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Units of Pressure

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

Footnotes

1. 1 BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

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Glossary

abbreviated electron configuration | An electron configuration that uses one of the noble gases to represent the core of electrons up to that element.

absolute zero | The minimum possible temperature, labeled 0 K (zero kelvins).

acid | An ionic compound of the H^+ cation dissolved in water.

acid dissociation constant | The equilibrium constant for the dissociation of a weak acid into ions.

acid salt | An ionic compound whose aqueous solution is slightly acidic.

activity series | A list of elements that will replace elements below them in single-replacement reactions.

actual yield | The amount that is actually produced in a chemical reaction.

addition reaction | The reaction of a halogen molecule across a C–C double or triple bond.

alkaline battery | A type of dry cell that contains an alkaline (i.e., basic) moist paste, rather than an acidic paste.

alkynes | An aliphatic hydrocarbon that contains a C–C triple bond.

alpha particle | A type of radioactive emission equivalent to a helium nucleus.

amphiprotic | A substance that can act as a proton donor or a proton acceptor.

angular momentum quantum number | An index that affects the energy and the spatial distribution of an electron in an atom. Represented by ℓ.

Aromatic hydrocarbons | A hydrocarbon that contains a benzene ring.

Arrhenius base | A compound that increases the hydroxide ion concentration in aqueous solution.

atmosphere | A unit of pressure equal to the average atmospheric pressure at sea level; defined as exactly 760 mmHg.

atom | The smallest piece of an element that maintains the identity of that element.

atomic bomb | A weapon that depends on a nuclear chain reaction to generate immense forces.

atomic mass | The weighted average of the masses of the isotopes that compose an element.

atomic mass unit | One-twelfth of the mass of a carbon-12 atom.

atomic number | The number of protons in an atom.

atomic radius | An indication of the size of the atom.

atomic symbol | A one- or two-letter representation of the name of an element.

autoionization constant of water | The product of the hydrogen ion and hydroxide ion concentrations.

autoionization of water | Water molecules act as acids (proton donors) and bases (proton acceptors) with each other to a tiny extent in all aqueous solutions.

balanced | A condition when the reactants and products of a chemical equation have the same number of atoms of all elements present.

base | A compound that increases the amount of OH^- ions in an aqueous solution.

basic salt | An ionic compound whose aqueous solution is slightly basic.

battery | A portable voltaic cell that generates electricity to power devices for our convenience.

beta particle | A type of radioactive emission equivalent to an electron.

boiling point elevation | The increase of a solution's boiling point because of the presence of solute.

boiling point elevation constant | The constant that relates the molality concentration of a solution and its boiling point change.

bond energy | The approximate amount of energy needed to bread a covalent bond.

Boyle's law | A gas law that relates pressure and volume at constant temperature and amount.

Brønsted-Lowry base | Any species that can accept a proton from another molecule.

buffer | A solution that resists dramatic changes in pH.

calorimetry | The process of measuring enthalpy changes for chemical reactions.

capacity | The amount of strong acid or base a buffer can counteract.

catalyst | A substance that increases the speed of a reaction.

chain reaction | An exponential growth in a phenomenon.

Charles's law | A gas law that relates volume and temperature at constant pressure and amount.

chemical bond | The connection between two atoms in a molecule.

chemical change | The process of demonstrating a chemical property.

chemical equilibrium | The point at which forward and reverse chemical reactions balance each other's progress.

chemical nomenclature | A very specific system for naming compounds, in which unique substances get unique names.

Chemical properties | A characteristic that describes how matter changes form in the presence of other matter.

chemistry | The study of the interactions of matter with other matter and with energy.

coefficient | The part of a number in scientific notation that is multiplied by a power of 10. OR A number in a chemical equation indicating more than one molecule of the substance.

cohesion | The tendency of a substance to interact with itself.

colligative properties | A property of solutions related to the fraction that the solute particles occupy in the solution, not their identity.

combined gas law | A gas law that combines pressure, volume, and temperature.

combustion reaction | A chemical reaction in which a reactant combines with oxygen to produce oxides of all other elements as products.

complete ionic equation | A chemical equation in which the dissolved ionic compounds are written as separated ions.

composition reaction | A chemical reaction in which a single substance is produced from multiple reactants.

compound | A combination of more than one element.

concentrated | A solution with a lot of solute.

concentration | The removal of solvent, which increases the concentration of the solute in the solution.

condensed structural formula | A listing of the atoms bonded to each C atom in a chain.

conjugate acid-base pairs | Two species whose formulas differ by only a hydrogen ion.

conversion factor | A fraction that can be used to convert a quantity from one unit to another.

covalent bond | A chemical bond formed by two atoms sharing electrons.

covalent network solids | A crystalline solid composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion.

crystalline solid | A solid with a regular, repeating three-dimensional structure.

curie (Ci) | A unit of radioactivity equal to 3.7×10^{10} decays/s.

Dalton's law of partial pressures | The total pressure of a gas mixture, msubPtot, is equal to the sum of the partial pressures of the components, P_i.

daughter isotope | The product left over from the parent isotope in a nuclear equation.

decomposition reaction | A chemical reaction in which a single substance becomes more than one substance.

degrees | The unit of temperature scales.

Density | A physical property defined as a substance's mass divided by its volume.

derived units | A unit that is a product or a quotient of a fundamental unit.

dilution equation | The mathematical formula for calculating new concentrations or volumes when a solution is diluted or concentrated.

dipole-dipole interactions | An intermolecular force caused by molecules with a permanent dipole.

dispersion force | An intermolecular force caused by the instantaneous position of an electron in a molecule.

dissociation | The process of an ionic compound separating into ions when it dissolves.

double bond | A covalent bond composed of two pairs of bonding electrons.

double-replacement reaction | A chemical reaction in which parts of two ionic compounds are exchanged.

dry cell | A modern battery that does not contain large amounts of aqueous solution.

dynamic equilibrium | 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.

electrolysis | The process of making a nonspontaneous redox reaction occur by forcing electricity into a cell.

electromagnetic spectrum | The full span of the possible wavelengths, frequencies, and energies of light.

electron affinity (EA) | The energy change when a gas-phase atom accepts an electron.

electron configuration | The representation of the organization of electrons in shells and subshells in an atom.

electron groups | A covalent bond of any type or a lone electron pair.

Electron-deficient molecules | A molecule with less than eight electrons in the valence shell of an atom.

electronegativity | A qualitative scale for judging how much atoms of any element attract electrons.

electroplating | The deposition of a thin layer of metal on an object for protective or decorative purposes.

element | A substance that cannot be broken down into simpler chemical substances by ordinary chemical means.

Energy | The ability to do work.

enthalpy change | The heat of a process at constant pressure; denoted ΔH.

enthalpy of formation | The enthalpy change for a formation reaction; denoted ΔHf.

enthalpy of fusion (or heat of fusion) | The amount of energy needed to change from a solid to a liquid or from a liquid to a solid.

enthalpy of sublimation | The amount of energy needed to change from a solid to a gas or from a gas to a solid.

enthalpy of vaporization | The amount of energy needed to change from a liquid to a gas or from a gas to a liquid.

equilibrium constant | A numerical value that relates to the ratio of products and reactants at equilibrium.

equivalence point | The point of the reaction when all the analyte has been reacted with the titrant.

exact number | A number from a defined relationship that technically has an infinite number of significant figures.

exothermic | A chemical reaction that has a negative change in enthalpy.

expanded valence shell molecules | A molecule with more than eight electrons in the valence shell of an atom.

Experiments | A test of the natural universe to see if a guess (hypothesis) is correct.

exponent | The raised number to the right of a 10 indicating the number of factors of 10 in the original number.

***f* block** | The columns of the periodic table in which *f* subshells are being occupied.

Formation reactions | A chemical reaction that forms one mole of a substance from its constituent elements in their standard states.

freezing point depression | The decrease of a solution's freezing point because of the presence of solute.

freezing point depression constant | The constant that relates the molality concentration of a solution and its freezing point change.

frequency | The number of cycles of light that pass a given point in one second.

fundamental units | One of the seven basic units of SI used in science.

Fusion | A nuclear process in which small nuclei are combined into larger nuclei, releasing energy.

gamma rays | A type of radioactive emission that is a very energetic form of electromagnetic radiation.

Geiger counter | An electrical device that detects radioactivity.

half reaction method | The method of balancing redox reactions by writing and balancing the individual half reactions.

half-life | The amount of time it takes for one-half of a radioactive isotope to decay.

Heat | The transfer of energy from one body to another due to a difference in temperature.

Hess's law | When chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way.

heterogeneous equilibrium | An equilibrium in which more than one phase of reactants or products is present.

hydrogen bonding | The very strong interaction between molecules due to H atoms being bonded to N, O, or F atoms.

hydrogenation reaction | The reaction of hydrogen across a C–C double or triple bond, usually in the presence of a catalyst.

hydrolysis | A reaction with water.

hydronium ion | The actual chemical species that represents a hydrogen ion.

hypothesis | An educated guess about how the natural universe works.

ideal gas | A gas that exactly follows the statements of the kinetic theory.

ideal gas law | A gas law that relates all four independent physical properties of a gas under any conditions.

indicator | A substance whose color change indicates the equivalence point of a titration.

ionic bond | The attraction between oppositely charged ions.

ionic compounds | A compound formed from positive and negative ions.

ionic formulas | The chemical formula for an ionic compound.

ionic solid | A crystalline solid composed of ions.

Ionization energy (IE) | The amount of energy required to remove an electron from an atom in the gas phase.

isolated system | A system that does not allow a transfer of energy or matter into or out of the system.

isomers | A molecule with the same molecular formula as another molecule but a different structure.

isothermal | A process that does not change the temperature.

joule | The SI unit of energy.

kelvin | The fundamental unit of temperature in SI.

kinetic theory of gases | The fundamental model that describes the physical properties of gases.

lattice energy | The measured strength of ionic bonding.

law | A specific statement that is thought to be never violated by the entire natural universe.

law of conservation of energy | The total energy of an isolated system does not increase or decrease.

law of mass action | The relationship of the amounts of reactants and products at equilibrium.

Le Chatelier's principle | If an equilibrium is stressed, then the reaction shifts to reduce the stress.

Lewis electron dot diagram | A representation of the valence electrons of an atom that uses dots around the symbol of the element.

limiting reagent | The reactant that runs out first.

line spectrum | An image that contains only certain colors of light.

lone electron pairs | A pair of electrons that does not make a covalent bond.

magnetic quantum number | The index that determines the orientation of the electron's spatial distribution. Represented by m_l.

mass number | The sum of the number of protons and neutrons in a nucleus.

mass-mass calculations | A calculation in which you start with a given mass of a substance and calculate the mass of another substance involved in the chemical equation.

Matter | Anything that has mass and takes up space.

meniscus | The curved surface a liquid makes as it approaches a solid barrier.

metallic solid | A solid with the characteristic properties of a metal.

modern atomic theory | The concept that atoms play a fundamental role in chemistry.

molality | The number of moles of solute per kilogram of solvent.

molar masses | The mass of 1 mol of a substance in grams.

molar volume | The volume of exactly 1 mol of a gas; equal to 22.4 L at STP.

Molarity | The number of moles of solute divided by the number of liters of solution.

mole | The number of things equal to the number of atoms in exactly 12 g of carbon-12; equals 6.022×10^{23} things.

mole fraction | The ratio of the number of moles of a component in a mixture divided by the total number of moles in the sample.

mole-mass calculation | A calculation in which you start with a given number of moles of a substance and calculate the mass of another substance involved in the chemical equation, or vice versa.

mole-mole calculation | A stoichiometry calculation when one starts with moles of one substance and convert to moles of another substance using the balanced chemical equation.

molecular formula | A formal listing of what and how many atoms are in a molecule.

molecular mass | The sum of the masses of the atoms in a molecule.

molecular solid | A crystalline solid whose components are covalently bonded molecules.

molecules | The smallest part of a substance that has the physical and chemical properties of that substance.

net ionic equation | A chemical equation with the spectator ions removed.

neutral salt | An ionic compound that does not affect the acidity of its aqueous solution.

neutralization reaction | The reaction of an acid and a base to produce water and a salt.

neutron | A subatomic particle with no charge.

nonpolar covalent bond | The equal sharing of electrons in a covalent bond.

normal boiling point | The characteristic temperature at which a liquid becomes a gas when the surrounding pressure is exactly 1 atm.

Nuclear energy | The controlled harvesting of energy from fission reactions.

nuclear equation | A chemical equation that emphasizes changes in atomic nuclei.

nuclear reactor | An apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes.

nucleus | The center of an atom that contains protons and neutrons.

numerical prefixes | A prefix used with a unit that refers to a multiple or fraction of a fundamental unit to make a more conveniently sized unit for a specific quantity.

octet rule | The trend that atoms like to have eight electrons in their valence shell.

Odd-electron molecules | A molecule with an odd number of electrons in the valence shell of an atom.

orbital | The specific set of principal, angular momentum, and magnetic quantum numbers for an electron.

osmotic pressure | The tendency of a solution to pass solvent through a semipermeable membrane due to concentration differences.

oxidation number | A number assigned to an atom that helps keep track of the number of electrons on the atom.

oxidation numbers | A number assigned to an atom that helps keep track of the number of electrons on the atom.

oxidation-reduction (or redox) reactions | A chemical reaction that involves the transfer of electrons.

partial pressure | The pressure that an individual gas in a mixture has.

parts per billion (ppb) | Ratio of mass of solute to total mass of sample times 1,000,000,000.

Pauli exclusion principle | No two electrons in an atom can have the same set of four quantum numbers.

percent yield | Actual yield divided by theoretical yield times 100% to give a percentage between 0% and 100%.

percentage composition by mass | Ratio of mass of solute to the total mass of a sample times 100.

periodic table | A chart of all the elements.

periodic trends | Variation of properties versus position on the periodic table.

pH | The negative logarithm of the hydrogen ion concentration.

pH scale | The range of values from 0 to 14 that describes the acidity or basicity of a solution.

photon | The name of a wave of light acting as a particle.

physical change | A change that occurs when a sample of matter changes one or more of its physical properties.

Physical properties | A characteristic that describes matter as it exists.

Planck's constant | The proportionality constant between the frequency and the energy of light.

pOH | The negative logarithm of the hydroxide ion concentration.

polar covalent bond | The unequal sharing of electrons in a covalent bond.

polyatomic ions | An ion that contains more than one atom.

precipitate | A solid that falls out of solution in a precipitation reaction.

Pressure | Force per unit area.

primary batteries | A battery that cannot be recharged.

products | A final substance in a chemical equation.

quantitative | A description of a specific amount of something.

quantized | When a quantity is restricted to having only certain values.

quantum mechanics | The theory of electrons that treats them as a wave.

rad | A unit of radioactive exposure equal to 0.01 J/g of tissue.

radioactive decay | The spontaneous change of a nucleus from one element to another.

radioactivity | Emanations of particles and radiation from atomic nuclei.

Raoult's law | The mathematical formula for calculating the vapor pressure of a solution.

rem | A unit of radioactive exposure that includes a factor to account for the type of radioactivity.

salt | Any ionic compound that is formed from a reaction between an acid and a base.

salt bridge | A part of a voltaic cell that contains a solution of some ionic compound whose ions migrate to either side of the voltaic cell to maintain the charge balance.

saturated hydrocarbons | A carbon compound with the maximum possible number of H atoms in its formula.

Science | The process of knowing about the natural universe through observation and experiment.

Scientific notation | An expression of a number using powers of 10.

secondary batteries | A battery that can be recharged.

semimetals (or metalloids) | An element that has properties of both metals and nonmetals.

semipermeable membrane | A thin membrane that will pass certain small molecules but not others.

shell | A term used to describe electrons with the same principal quantum number.

significant figures | The limit of the number of places a measurement can be properly expressed with.

single bond | A covalent bond composed of one pair of electrons.

single-replacement reaction | A chemical reaction in which one element is substituted for another element in a compound.

solubility | The maximum amount of a solute that can be dissolved in a given amount of a solvent.

solubility product constant | The equilibrium constant for a compound normally considered insoluble.

solubility rules | General statements that predict which ionic compounds dissolve and which do not.

solute | The minor component of a solution.

solution | Another name for a homogeneous mixture.

specific heat capacity | The proportionality constant between heat, mass, and temperature change; also called specific heat.

spectator ions | An ion that does nothing in the overall course of a chemical reaction.

spin quantum number | The index that indicates one of two spin states for an electron. Represented by m_s.

spontaneous fission (or fission) | The breaking apart of an atomic nucleus into smaller nuclei.

Standard notation | A straightforward expression of a number.

standard reduction potentials | The voltage of a reduction half reaction relative to the hydrogen half reaction.

Standard temperature and pressure (STP) | A set of benchmark conditions used to compare other properties of gases; about 1 atm for pressure and 273 K for temperature.

stoichiometry | The relating of one chemical substance to another using a balanced chemical reaction.

subshell | A term used to describe electrons in a shell that have the same angular momentum quantum number.

substance | Matter that has the same physical and chemical properties throughout.

supersaturated | A unstable solution with more than the normal maximum amount of solute in it.

Surface tension | An effect caused by an imbalance of forces on the atoms at the surface of a liquid.

surrounding atoms | An atom that makes covalent bonds to the central atom(s).

theoretical yield | An amount that is theoretically produced as calculated using the balanced chemical reaction.

theory | A general statement that explains a large number of observations.

thermochemical equation | A chemical equation that includes an enthalpy change.

titration | A chemical reaction performed quantitatively to determine the exact amount of a reagent.

torr | Another name for a millimeter of mercury.

tracer | A substance that can be used to follow the pathway of that substance through a structure.

triple bond | A covalent bond composed of three pairs of bonding electrons.

unsaturated | A solution with less than the maximum amount of solute dissolved in it.

valence shell | The highest-numbered shell in an atom that contains electrons.

valence shell electron pair repulsion (VSEPR) | The general concept that estimates the shape of a simple molecule.

van't Hoff factor | The number of particles each solute formula unit breaks apart into when it dissolves.

vapor | Material in the gas phase due to evaporation.

vapor pressure | The partial pressure exerted by evaporation of a liquid.

vapor pressure depression | The decrease of a solution's vapor pressure because of the presence of a solute.

voltage | The tendency for electrons to go from one half cell to another.

voltaic (galvanic) cell | An apparatus that allows for useful electrical work to be extracted from a redox reaction.

weak acid | Any acid that is less than 100% dissociated into ions in aqueous solution.

weak base | Any base that is less than 100% dissociated into ions in aqueous solution.

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