CHEM 1510: INTRODUCTORY COLLEGE CHEMISTRY



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Introductory College Chemistry

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Detailed Licensing

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CHAPTER OVERVIEW

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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 ${}_{2}^{4}\mathrm{He}$. In the definition of the atomic mass unit, the “most common isotope of carbon”, ${}_{6}^{12}\mathrm{C}$, 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 $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$.

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, $^{35}_{17}\text{Cl}$ was the most common isotope with an abundance of 75.77% and $^{37}_{17}\text{Cl}$ 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: 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 1.3.1).

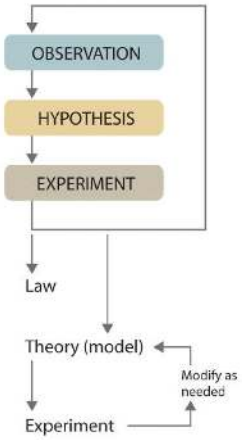


Figure 1.3.1: The Steps in the Scientific Method.

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 1.3.1 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 1.3.1

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 1.3.1

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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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.

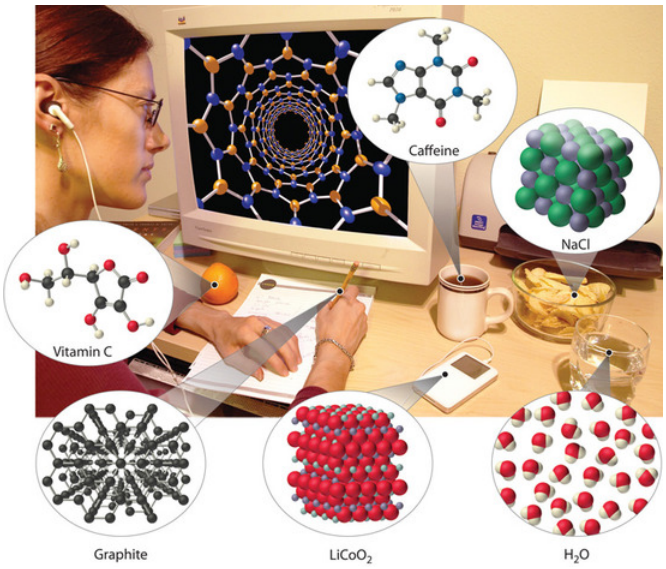


Figure 1.5.1: Chemistry in Everyday Life. Although most people do not recognize it, chemistry and chemical compounds are crucial ingredients in almost everything we eat, wear, and use.

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: 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 **1.6.1**: 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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1.7: 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 1.7.1). 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.

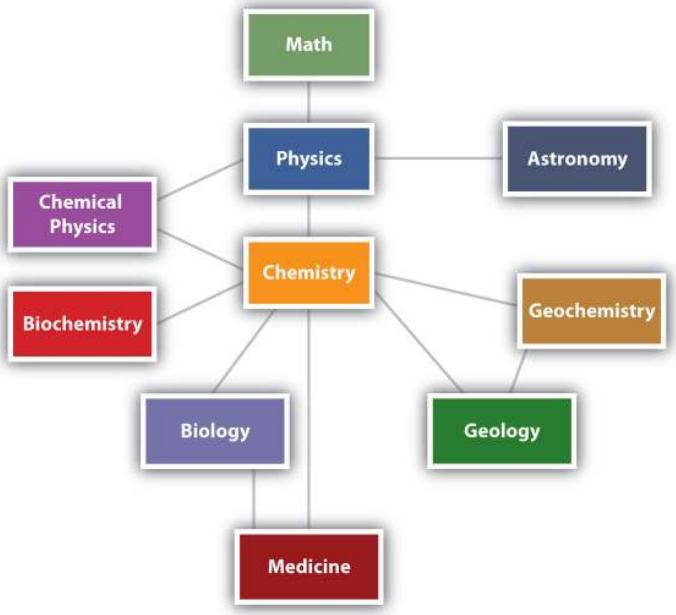


Figure 1.7.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

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 1.7.1 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 1.7.1: 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 1.7.1

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 1.7.2: (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 1.7.3). 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 1.7.3: 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 1.7.4).

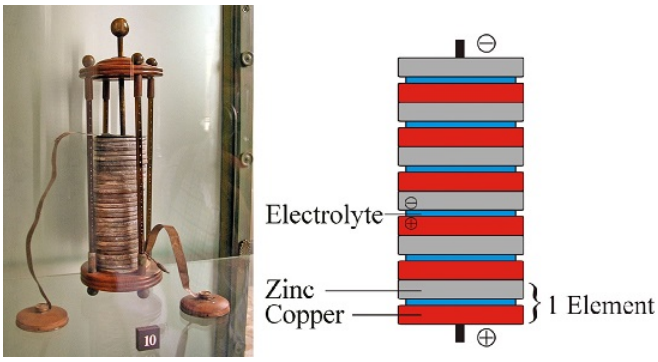


Figure 1.7.4: Battery developed by Volta. (CC BY-SA 3.0; (left) GuidoB and (right) Kkkdc).

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 1.7.5). 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 1.7.5: 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.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

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: Scientific Notation - Writing Large and Small Numbers
2.2: The Basic Units of Measurement
2.3: Significant Figures - Writing Numbers to Reflect Precision
2.4: Significant Figures in Calculations
2.5: Problem Solving and Unit Conversions
2.6: Solving Multi-step Conversion Problems
2.7: Units Raised to a Power
2.8: Temperature - Random Motion of Molecules and Atoms
2.9: Density
2.E: Measurement and Problem Solving (Exercises)

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2.1: 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 ($1 \le N < 10$), and n is a positive or negative integer ($10^0 = 1$). The number 10 is called the base because it is this number that is raised to the power n. Although a base number may have values other than 10, the base number in scientific notation is always 10.

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

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

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example 2.1.1.

Example 2.1.1: 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

	Explanation	Answer
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 $2.1.2$ illustrates how to do this.

Example 2.1.2: 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.	4.8
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.	6.0

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 2.1.3.

Example 2.1.3: 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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2.2: 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).

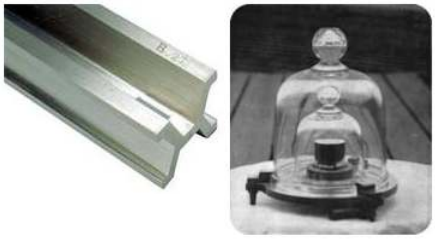


Figure 2.2.1: Meter standard (left) and Kilogram standard (right).

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 2.2.1.

Table 2.2.1: 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.

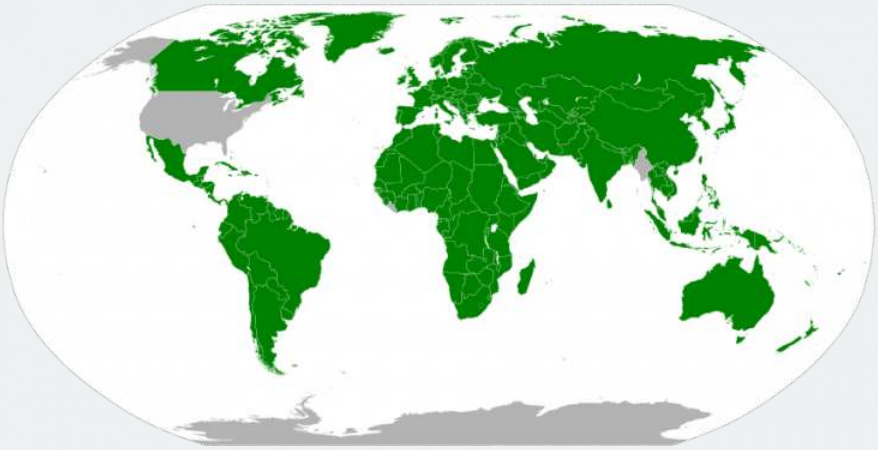


Figure 2.2.1: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

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 $\mu\varepsilon\gamma\alpha\varsigma$, meaning "great". Table $2.2.2$ 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 2.2.2: SI Prefixes

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

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

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs 6.5 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 2.2.1: 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 2.2.1

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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2.3: 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.

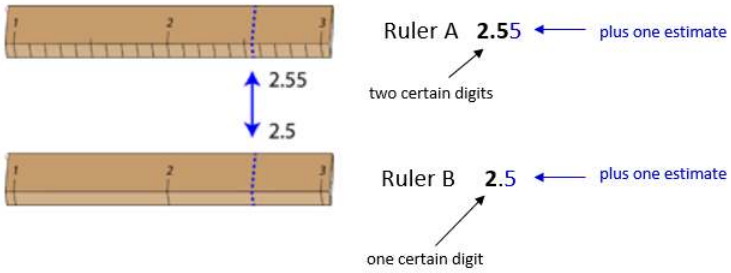


Figure 2.3.1: Measurement with two different rulers.
Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

Measurement Uncertainty

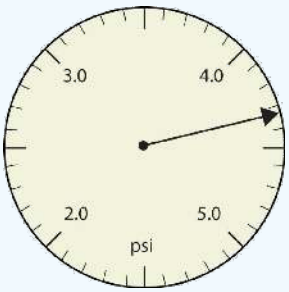
Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest $0.1\ \text{g}$, other highly sensitive balances are 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.

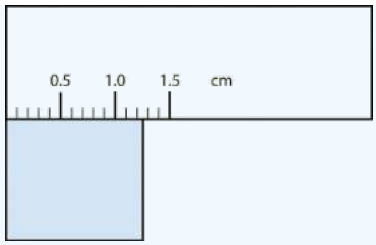
Example 2.3.1: Reporting Measurements to the Proper Number of Significant Figures

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

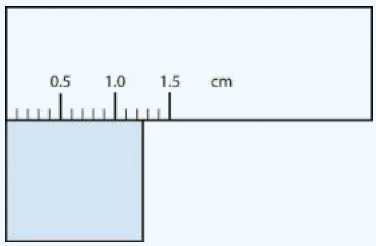
Solutions

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

https://chem.libretexts.org/@go/page/471938

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

	Explanation	Answer
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

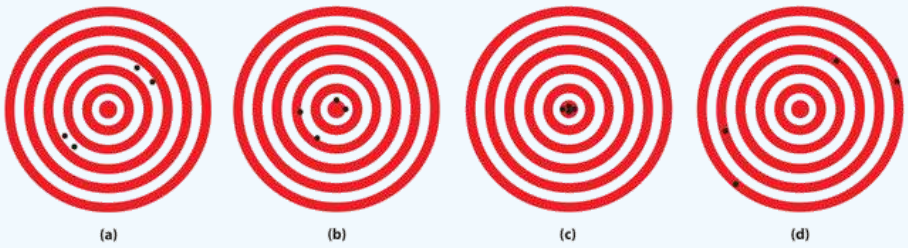
Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal 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.

$$\begin{array}{r} 1.2 \\ +\ 4.41 \\ \hline 5.61 \end{array}$$

↑ limit final answer to the tenths column: 5.6

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

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

$$\begin{array}{r} 77.2 \\ +\ 10.46 \\ \hline 87.66 \end{array}$$

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

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

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: 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 2.5.1).

Table 2.5.1: 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 2.5.1. 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 2.5.1 shows a concept map for constructing a proper conversion.

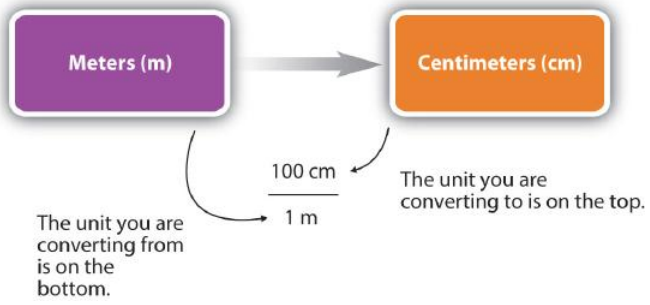


Figure 2.5.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

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.

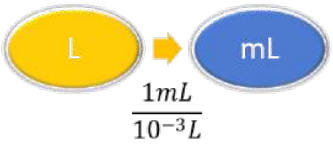
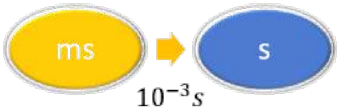
SIGNIFICANT FIGURES IN CONVERSIONS

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 2.5.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

	Example 2.5.1	**Example 2.5.2**
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.	$4.7\ \cancel{\text{L}} \times \frac{1\ \text{mL}}{10^{-3}\ \cancel{\text{L}}} = 4,700\ \text{mL}$ or $4.7\ \cancel{\text{L}} \times \frac{1,000\ \text{mL}}{1\ \cancel{\text{L}}} = 4,700\ \text{mL}$ or 4.7 x 10^3 2SF, not ambiguous	$18\ \cancel{\text{ms}} \times \frac{10^{-3}\ \text{s}}{1\ \cancel{\text{ms}}} = 0.018\ \text{s}$ or $18\ \cancel{\text{ms}} \times \frac{1\ \text{s}}{1,000\ \cancel{\text{ms}}} = 0.018\ \text{s}$
Think about your result.	The amount in 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 2.5.1

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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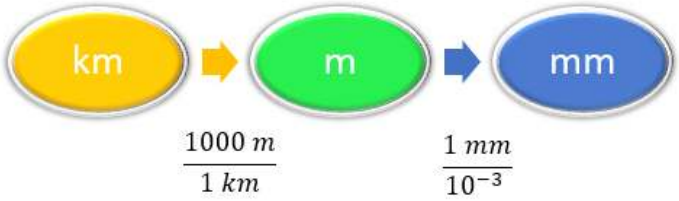
2.6: SOLVING MULTI-STEP CONVERSION PROBLEMS

MULTIPLE CONVERSIONS

Sometimes you will have to perform more than one conversion to obtain the desired unit. For example, suppose you want to convert 54.7 km into millimeters. We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence. We first convert the given amount in km to the base unit, which is meters. We know that 1,000 m =1 km.

Then we convert meters to mm, remembering that 1 mm = 10^{-3} m.

CONCEPT MAP



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

CALCULATION

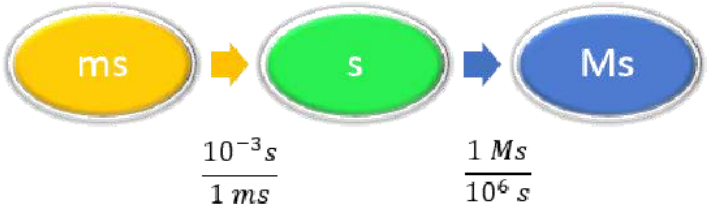
$$54.7\ \cancel{\text{km}} \times \frac{1{,}000\ \cancel{\text{m}}}{1\ \cancel{\text{km}}} \times \frac{1\ \text{mm}}{10^{-3}\cancel{\text{m}}} = 54{,}700{,}000\ \text{mm}$$
$$= 5.47 \times 10^{7}\ \text{mm}$$

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

✔ EXAMPLE 2.6.1: UNIT CONVERSION

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

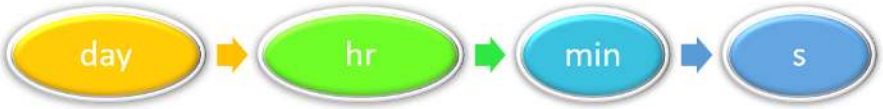
SOLUTION

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities	$1ms = 10^{-3}s$ $1Ms = 10^{6}s$
Prepare a concept map.	 Convert milliseconds to seconds to microseconds: use conversion factors 0.001 second per millisecond and 1 microsecond per 1 million seconds
Calculate.	$58.2\ \cancel{\text{ms}} \times \frac{10^{-3}\ \cancel{\text{s}}}{1\ \cancel{\text{ms}}} \times \frac{1\ \text{Ms}}{1{,}000{,}000\ \cancel{\text{s}}} = 0.0000000582\ \text{Ms}$ $= 5.82 \times 10^{-8}\ \text{Ms}$ Neither conversion factor affects the number of significant figures in the final answer.

EXAMPLE 2.6.2: UNIT CONVERSION

How many seconds are in a day?

Solution

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 1 day Find: s
List other known quantities.	1 day = 24 hours 1 hour = 60 minutes 1 minute = 60 seconds
Prepare a concept map.	 $\frac{24\text{hr}}{1\text{ day}}$ $\frac{60\text{min}}{1\text{ hr}}$ $\frac{60\text{ s}}{1\ min}$ Convert day to hour to minute to second: use conversion factors 24 hours per day, 60 minutes per hour, and 60 seconds per minute
Calculate.	$1\text{ d} \times \frac{24\text{ hr}}{1\text{ d}} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ s}}{1\text{ min}} = 86,400\text{ s}$

EXERCISE 2.6.1

Perform each conversion in one multi-step calculation.

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

Answer a

$4.3007 \times 10^{-11} kg$

Answer b

$83.75\ ft$

Answer c

$19\ km$

CAREER FOCUS: PHARMACIST

A pharmacist dispenses drugs that have been prescribed by a doctor. Although that may sound straightforward, pharmacists in the United States must hold a doctorate in pharmacy and be licensed by the state in which they work. Most pharmacy programs require four years of education in a specialty pharmacy school. Pharmacists must know a lot of chemistry and biology so they can understand the effects that drugs (which are chemicals, after all) have on the body. Pharmacists can advise physicians on the selection, dosage, interactions, and side effects of drugs. They can also advise patients on the proper use of their medications, including when and how to take specific drugs properly. Pharmacists can be found in drugstores, hospitals, and other medical facilities. Curiously, an outdated name for pharmacist is *chemist*, which was used when pharmacists formerly did a lot of drug preparation, or *compounding*. In modern times, pharmacists rarely compound their own drugs, but their knowledge of the sciences, including chemistry, helps them provide valuable services in support of everyone's health.



A woman consulting with a pharmacist. (Public Domain; Rhoda Baer via National Cancer Institute, an agency that is part of the National Institutes of Health.)

SUMMARY

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

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2.7: Units Raised to a Power

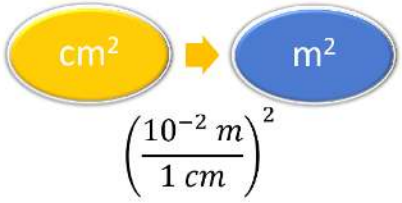
Learning Objectives

- To convert a value reported in one unit raised to a power of 10, to a corresponding value in a different unit raised to the same power of 10, using conversion factors.

Conversion factors for area and volume can also be produced by the dimensional analysis method. Just remember that if a quantity is raised to a power of 10, both the number and the unit must be raised to the same power of 10. For example, to convert 1500 cm^2 to m^2, we need to start with the relationship between centimeter and meter. We know that 1 cm = 10^{-2} m or 100 cm =1 m, but since we are given the quantity in 1500 cm^2, then we have to use the relationship:

$$1\,cm^2 = (10^{-2}\,m)^2 = 10^{-4}\,m^2$$

CONCEPT MAP



To convert centimeters squared to meters squared, use the conversion factor 0.01 meters per 1 centimeter, squared overall

CALCULATION

$$1500\ \text{cm}^2 \times \left(\frac{10^{-2}\ \text{m}}{1\ \text{cm}}\right)^2 = 0.15\ \text{m}^2$$

or

$$1500\ \text{cm}^2 \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^2 = 0.15\ \text{m}^2$$

or

$$1500\ \text{cm}^2 \times \frac{1\ \text{m}^2}{10,000\ \text{cm}^2} = 0.15\ \text{m}^2$$

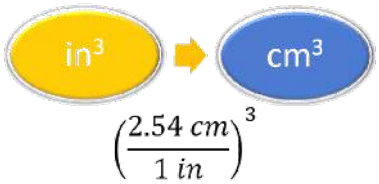
Example 2.7.1: Volume of a Sphere

What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?

Solution

Solution for Example 2.8.1

Steps for Problem Solving	What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?
Identify the "given" information and what the problem is asking you to "find."	Given: radius = 4.30 in Find: cm^3 (volume)
Determine other known quantities.	Volume of a sphere: V = $\frac{4}{3} \times \pi \times r^3$ = $\frac{4}{3} \times 3.1416 \times (4.30\underline{in})^3$ = $333.04 in^3$

Steps for Problem Solving	What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?
Prepare a concept map.	 To convert inches cubed to centimeters cubed, use conversion factor 2.54 centimeters per 1 inch, cubed overall
Calculate.	$333.04\ \cancel{in^3}\left(\frac{2.54cm}{1\ \cancel{in}}\right)^3 = 5.46 \times 10^3 cm^3$
Think about your result.	A centimeter is a smaller unit than an inch, so the answer in cubic centimeters is larger than the given value in cubic inches.

? Exercise 2.7.1

Lake Tahoe has a surface area of 191 square miles. What is the area in square km (km^2)?

Answer

495 km^2

Contributions & Attributions

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2.8: 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 2.8.1: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

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



Figure 2.8.2: 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 $32^{\circ}\mathrm{F}$ and the boiling point as $212^{\circ}\mathrm{F}$. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Scale

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

The Kelvin Scale

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

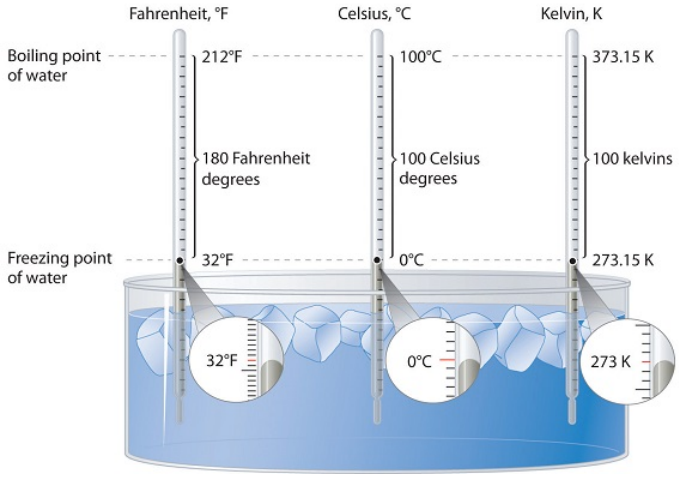


Figure 2.8.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (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:

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

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

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:

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

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

Example 2.8.1: Temperature Conversions

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

Solution

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

$$^\circ C = \frac{(103.5^\circ F - 32)}{1.8} \tag{2.8.1}$$

$$= 39.7\,^\circ C \tag{2.8.2}$$

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

$$K = 39.7\ ^{\circ}C + 273.15 \quad (2.8.3)$$
$$= 312.9\ K \quad (2.8.4)$$

? Exercise 2.8.1

Convert each temperature to °C and °F.

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

Answer (a)

5527 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).

Contributions & Attributions

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2.9: 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

$$\rho = \frac{m}{V} \tag{2.9.1}$$

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 2.9.1. 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 2.9.1: 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 2.9.1: 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 2.9.1:

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

Exercise 2.9.1

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:

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

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

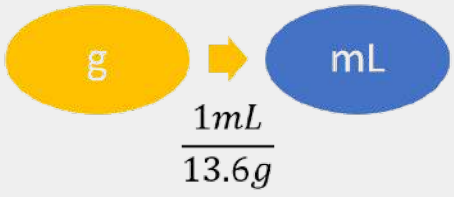
> *Density can be used as a conversion factor between mass and volume.*

Example 2.9.2: 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.	$0.750\ \cancel{\text{g}} \times \frac{1\ \text{mL}}{13.6\ \cancel{\text{g}}} = 0.055147...\ \text{mL} \approx 0.0551\ \text{mL}$ We have limited the final answer to three significant figures.

? Exercise 2.9.2

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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2.E: Measurement and Problem Solving (Exercises)

2.1: Measuring Global Temperatures

2.2: Scientific Notation: Writing Large and Small Numbers

2.3: Significant Figures: Writing Numbers to Reflect Precision

1. Define *significant figures*. Why are they important?
2. Define the different types of zeros found in a number and explain whether or not they are significant.
3. How many significant figures are in each number?
    a. 140
    b. 0.009830
    c. 15,050
    d. 221,560,000
    e. 5.67×10^{3}
    f. 2.9600×10^{-5}
4. How many significant figures are in each number?
    a. 1.05
    b. 9,500
    c. 0.0004505
    d. 0.00045050
    e. 7.210×10^{6}
    f. 5.00×10^{-6}
5. Round each number to three significant figures.
    a. 34,705
    b. 34,750
    c. 34,570

2.4: Significant Figures in Calculations

2.5: The Basic Units of Measurement

2.6: Problem Solving and Unit Conversions

2.7: Solving Multi-step Conversion Problems

2.8: Units Raised to a Power

2.9: Density

2.10: Numerical Problem-Solving Strategies and the Solution Map

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CHAPTER OVERVIEW

3: Matter

3.1: What is Matter?
3.2: Classifying Matter According to Its State—Solid, Liquid, and Gas
3.3: Classifying Matter According to Its Composition
3.4: Differences in Matter- Physical and Chemical Properties
3.5: Changes in Matter - Physical and Chemical Changes
3.6: Conservation of Mass - There is No New Matter
3.7: Energy and Chemical and Physical Change

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3.1: 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 3.1.1: 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".

Contributions & Attributions

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3.2: 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 $0^{o}C$), it is a solid. When at "normal" temperatures (between $0^{o}C$ and $100^{o}C$), it is a liquid. While at temperatures above $100^{o}C$, 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**.

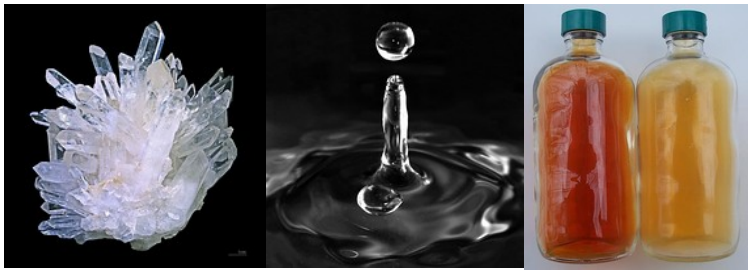


Figure 3.2.1: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

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 3.2.2 shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

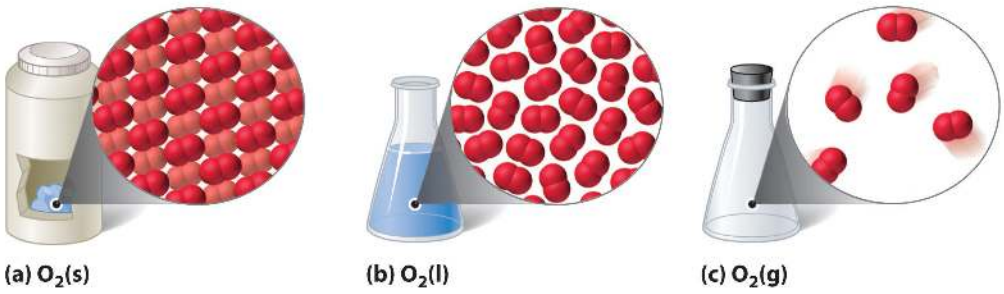


Figure 3.2.2: A Representation of the Solid, Liquid, and Gas States. (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 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 $-39^{\circ}\mathrm{C}$, 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 3.2.3. 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.

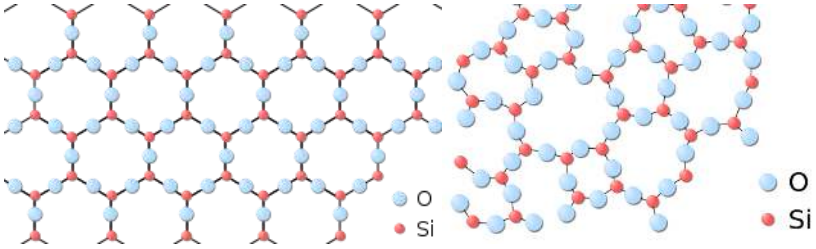


Figure 3.2.3: (left) The periodic crystalline lattice structure of quartz SiO_2 in two-dimensions. (right) The random network structure of glassy SiO_2 in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in 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* 3.2.1** *: Mercury boiling to become a gas.*

If we heat liquid mercury to its boiling point of 357°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 3.2.1: 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 3.2.1

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 3.2.1

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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3.3: 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 3.3.1). 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.

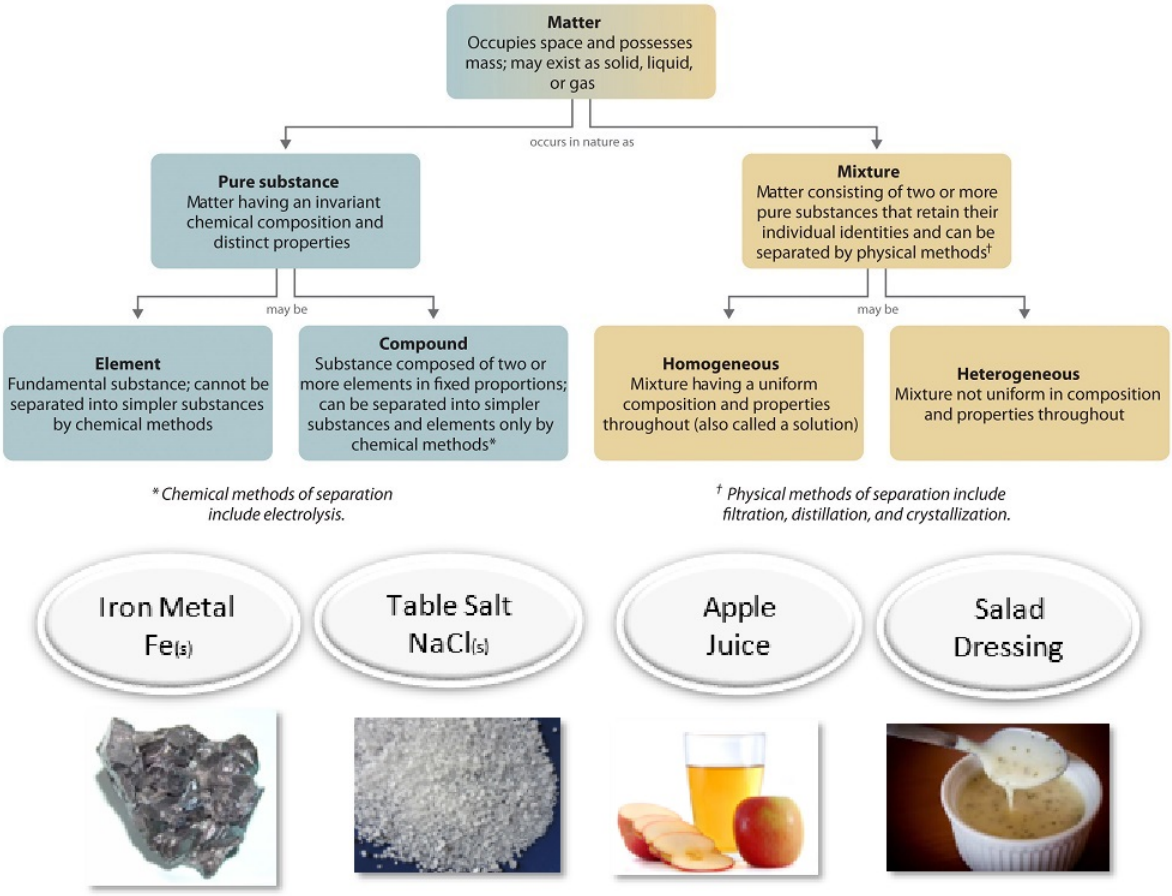


Figure 3.3.1: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

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 3.3.1

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

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

Given: a chemical substance

Asked for: its classification

Strategy:

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 3.3.1

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

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

Answer a:
homogeneous mixture (solution)

Answer b:
element

Answer c:
heterogeneous mixture

Answer d:
compound

Example 3.3.2

How would a chemist categorize each example of matter?

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

Solution

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of 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 3.3.2

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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3.4: 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 3.4.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table 3.4.1: Densities of Common Substances

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

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



Figure 3.4.1: 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 3.4.2: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure 3.4.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table 3.4.2: Contrasting Physical and Chemical Properties

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

Example 3.4.1

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 3.4.1A

Which of the following is a physical property of matter?

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

Answer

c

Exercise 3.4.1B

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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3.5: 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 3.5.1: 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 3.5.2: 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 3.5.1

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: $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$

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 3.5.1

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.

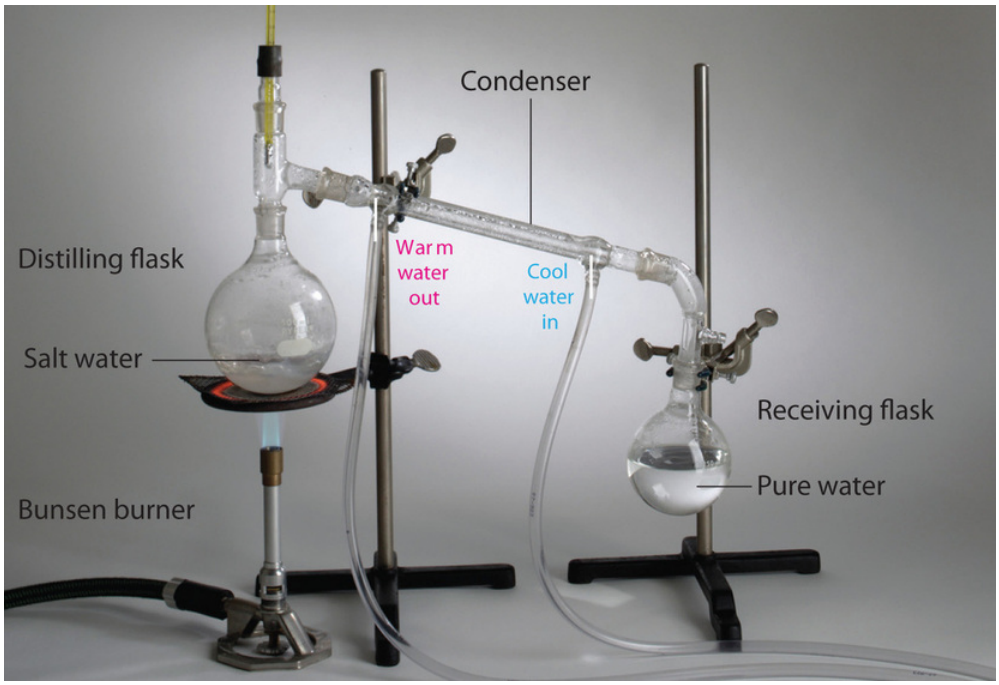


Figure 3.5.3: *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the 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 3.5.4). 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.

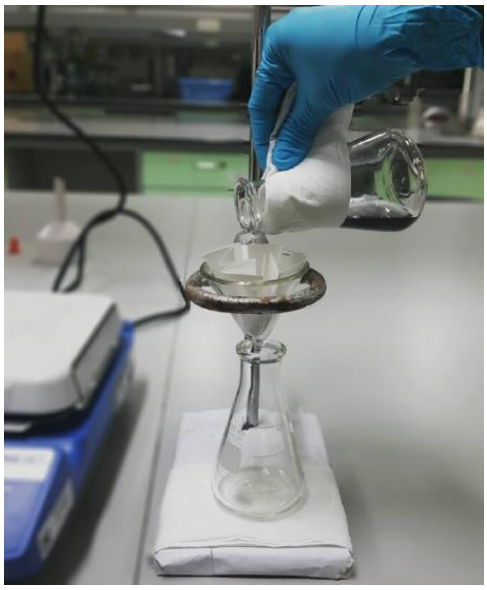


Figure 3.5.4: *Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

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.

Contributions & Attributions

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- Boundless (www.boundless.com)

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3.6: 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 3.6.1 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.

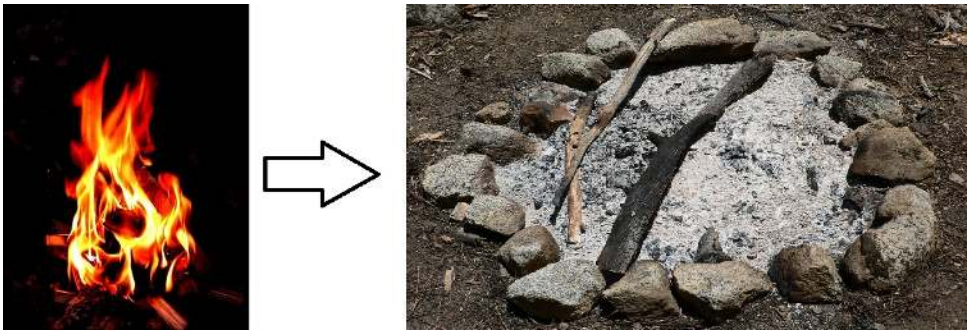


Figure 3.6.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). (CC BY-SA 2.5; Einar Helland Berger for fire and Walter Siegmund for ash).

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 3.6.1). 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 3.6.1: 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 3.6.1

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 3.6.1

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.

Contributions & Attributions

- Binod Shrestha (University of Lorraine)

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3.7: 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.

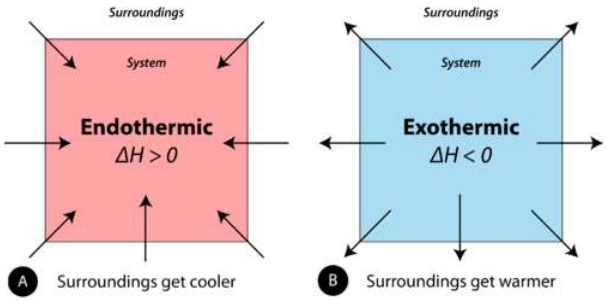


Figure 3.7.1: (A) Endothermic reaction. (B) Exothermic reaction.

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 3.7.1

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 3.7.1

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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CHAPTER OVERVIEW

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4.11: Looking for Patterns - The Periodic Table
4.12: Ions - Losing and Gaining Electrons

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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).

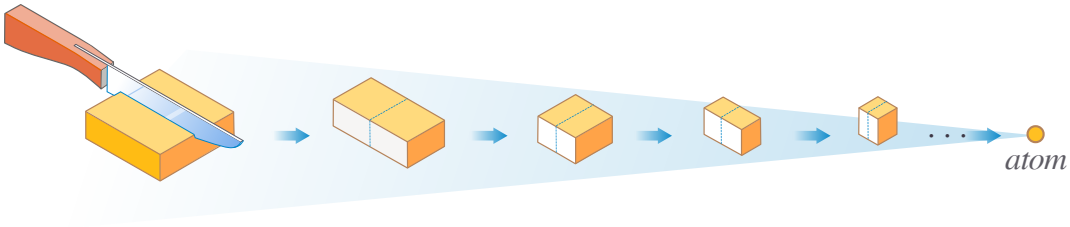


Figure 4.1.1: Democritus argued that matter, like an aluminum block, cannot be repeatedly cut in half perpetually. At some point, a limit is reached before the substance can no longer be called "aluminum"; this is the atomic limit. (CC BY-NC; Ümit Kaya via LibreTexts)

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: The Elements

Learning Objectives

- Define a chemical element and give examples of the abundance of different elements.
- Represent a chemical element with a chemical symbol.

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure 4.2.1 shows some of the chemical elements.



Figure 4.2.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Abundance

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90% of atoms), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect.

Table 4.2.1: Elemental Composition of Earth

Earth's Crust		Earth (overall)	
Element	**Percentage**	**Element**	**Percentage**
oxygen	46.1	iron	34.6
silicon	28.2	oxygen	29.5
aluminum	8.23	silicon	15.2
iron	5.53	magnesium	12.7
calcium	4.15	nickel	2.4
sodium	2.36	sulfur	1.9
magnesium	2.33	all others	3.7
potassium	2.09		
titanium	0.565		
hydrogen	0.14		
phosphorus	0.105		
all others	0.174		

Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 14–17.

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen,

the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table 4.2.1 lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table 4.2.2 lists the relative abundances of elements in the human body. If you compare Table 4.2.1 and Table 4.2.2, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 4.2.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table 4.2.2: Elemental Composition of a Human Body

Element	Percentage by Mass
oxygen	61
carbon	23
hydrogen	10
nitrogen	2.6
calcium	1.4
phosphorus	1.1
sulfur	0.20
potassium	0.20
sodium	0.14
chlorine	0.12
magnesium	0.027
silicon	0.026
iron	0.006
fluorine	0.0037
zinc	0.0033
all others	0.174

Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 7–24.

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

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

dropped, causing fish to die in large numbers. This process, called *eutrophication*, is considered a negative environmental impact.

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

Names and Symbols

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

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

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 4.2.3 lists the names and symbols of some of the most familiar elements.

Table 4.2.3: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

†The symbol for tungsten comes from its German name—*wolfram*.

lithium	Li	zirconium	Zr

*The symbol comes from the Latin name of element.

†The symbol for tungsten comes from its German name—*wolfram*.

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

Example 4.2.1

Write the chemical symbol for each element without consulting Table 4.2.3 "Element Names and Symbols".

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

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

Exercise 4.2.1

Write the chemical symbol for each element without consulting Table 4.2.3.

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

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

Example 4.2.2

What element is represented by each chemical symbol?

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

Answer a

sodium

Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

Exercise 4.2.2

What element is represented by each chemical symbol?

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

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Concept Review Exercises

1. What is an element?
2. Give some examples of how the abundance of elements varies.
3. Why are chemical symbols so useful? What is the source of the letter(s) for a chemical symbol?

Answers

1. An element is the basic chemical building block of matter; it is the simplest chemical substance.
2. Elements vary from being a small percentage to more than 30% of the atoms around us.
3. Chemical symbols are useful to concisely represent the elements present in a substance. The letters usually come from the name of the element.

Key Takeaways

- All matter is composed of elements.
- Chemical elements are represented by a one- or two-letter symbol.

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4.3: 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 4.3.1: (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.

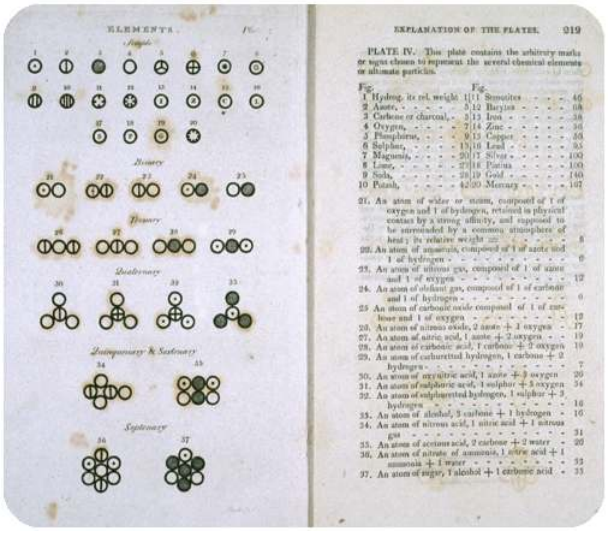
The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 4.3.1), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms 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.

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 4.3.2: 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 4.3.1, control of individual atoms can be use used create animations.



Video 4.3.1: A Boy And His Atom: The World's Smallest Movie.

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

Summary

- 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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4.4: 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 4.4.1: 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.

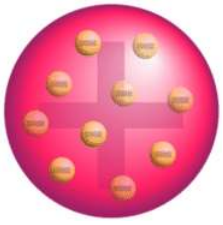


Figure 4.4.2: The "plum pudding" model.

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.

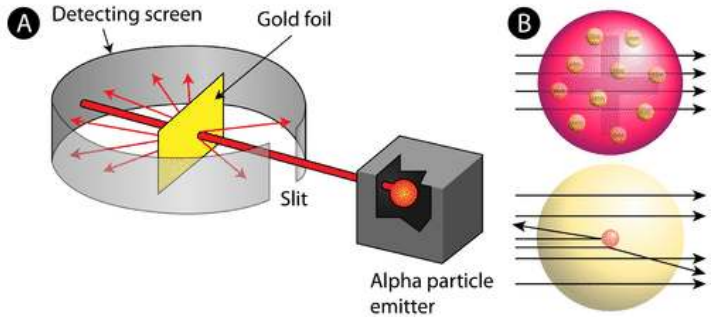


Figure 4.4.3: (A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding model (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.

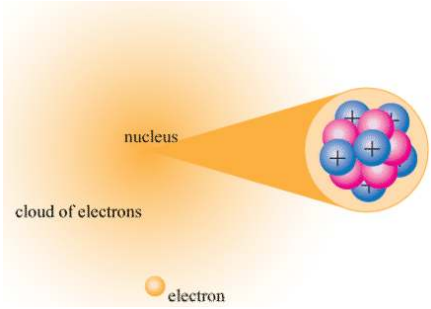


Figure 4.4.4: The nuclear atom.

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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4.5: 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).

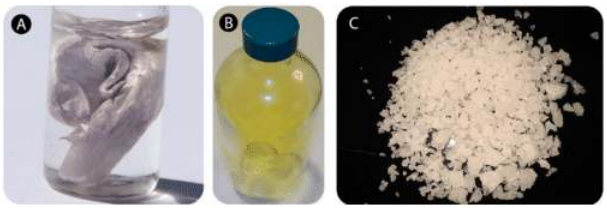


Figure 4.5.1: (A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine.

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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4.6: Chemical Formulas - How to Represent Compounds

Learning Objectives

- Determine the number of different atoms in a formula.
- Define chemical formula, molecular formula, and empirical formula.

A **chemical formula** is an expression that shows the elements in a compound and the relative proportions of those elements. Water is composed of hydrogen and oxygen in a 2:1 ratio. The chemical formula for water is H_2O. Sulfuric acid is one of the most widely produced chemicals in the United States and is composed of the elements hydrogen, sulfur, and oxygen. The chemical formula for sulfuric acid is H_2SO_4.

Certain groups of atoms are bonded together to form what is called a polyatomic ion that acts as a single unit. Polyatomic ions are discussed in more detail in Section 5.5. Polyatomic ions are enclosed in parenthesis followed by a subscript if more than one of the same ion exist in a chemical formula. The formula $Ca_3(PO_4)_2$ represents a compound with the following:

$$3 \text{ Ca atoms} + 2 \ PO_4^{3-} \text{ ions}$$

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

$$Ca_3(PO_4)_2$$

$$3 \text{ Ca} + 2 \text{ x1 P} + 2 \text{ x 4 O} = 3 \text{ Ca atoms} + 2 \text{ P atoms} + 8 \text{ O atoms}$$

Molecular Formula

A **molecular formula** is a chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound. Ammonia is a compound of nitrogen and hydrogen as shown below:

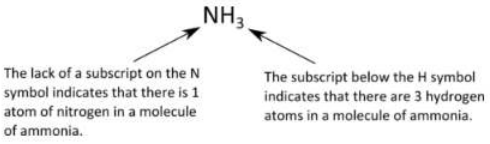


Figure 4.6.1: The molecular formula for ammonia. NH3. There is one atom of nitrogen and 3 atoms of hydrogen in a molecule of ammonia.

Note from the example that there are some standard rules to follow in writing molecular formulas. The arrangements of the elements depend on the particular structure, which is not of concern at this point. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write N_3H for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

Empirical Formula

An **empirical formula** is a formula that shows the elements in a compound in their lowest whole-number ratio. Glucose is an important simple sugar that cells use as their primary source of energy. Its molecular formula is $C_6H_{12}O_6$. Since each of the subscripts is divisible by 6, the empirical formula for glucose is CH_2O. When chemists analyze an unknown compound, often the first step is to determine its empirical formula.

- molecular formula: $C_6H_{12}O_6$
- empirical formula: CH_2O

There are a great many compounds whose molecular and empirical formulas are the same. If the molecular formula cannot be simplified into a smaller whole-number ratio, as in the case of H_2O or P_2O_5, then the empirical formula is also the molecular formula.

Summary

- A chemical formula is an expression that shows the elements in a compound and the relative proportions of those elements.
- If only one atom of a specific type is present, no subscript is used.
- For atoms that have two or more of a specific type of atom present, a subscript is written after the symbol for that atom.
- Polyatomic ions in chemical formulas are enclosed in parentheses followed by a subscript if more than one of the same type of polyatomic ion exist.
- Molecular formulas do not indicate how the atoms are arranged in the molecule.
- The empirical formula tells the lowest whole-number ratio of elements in a compound. The empirical formula does not show the actual number of atoms.

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4.7: 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 4.7.1: 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 4.7.1: 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 4.7.1 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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4.8: 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 4.8.1: 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 4.8.1). 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 4.8.1: 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 4.8.1). 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 4.8.1).

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.)

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

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

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

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 4.8.2.

Table 4.8.2: *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

Chemical Symbol	Name	Latin Name
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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4.9: 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 4.9.1. 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.

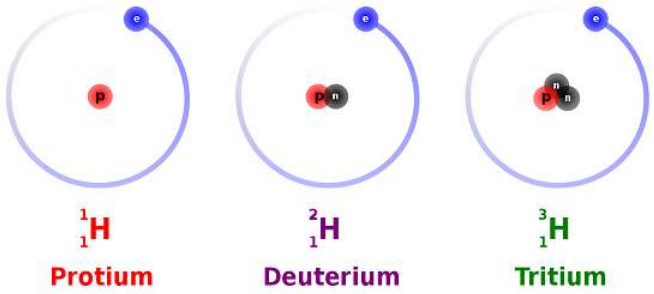


Figure 4.9.1: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

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 4.9.1: 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

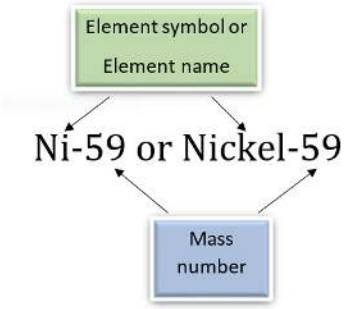
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

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

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

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 4.9.2: Potassium-40

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

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 4.9.3: 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 4.9.3

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

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

Answer a:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 neutrons

Answer c:

20 protons, 20 electrons, 25 neutrons

Answer d:

38 protons, 38 electrons, 52 neutrons

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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4.10: 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 4.10.1: 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 4.10.2: 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 $\mathbf{20.17}$ 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 $4.10.1$, and the atomic mass of neon (symbol Ne) is 20.8, which is what we calculated in Example $4.10.2$ 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 4.10.1

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 amu Another 24.23% of the atoms are Cl-37, with a mass of 36.97 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.

4.10: Atomic Mass - The Average Mass of an Element's Atoms is shared under a CK-12 license and was authored, remixed, and/or curated by Marisa Alviar-Agnew & Henry Agnew.

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4.11: 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 4.11.1. 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.

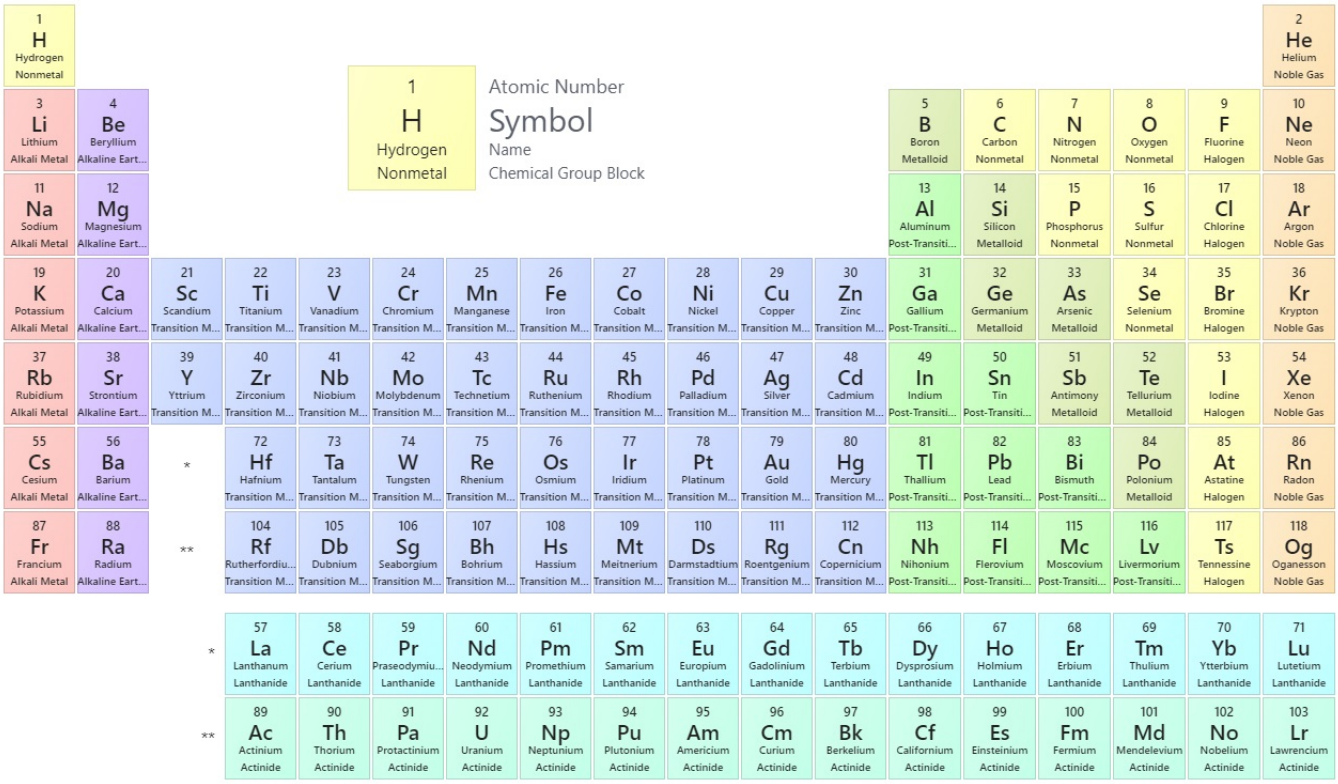


Figure 4.11.1: A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number. An interactive Periodic table can be found Periodic Table of Elements. (Public Domain; PubChem via NIH)

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 4.11.2. 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 4.11.2, 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.

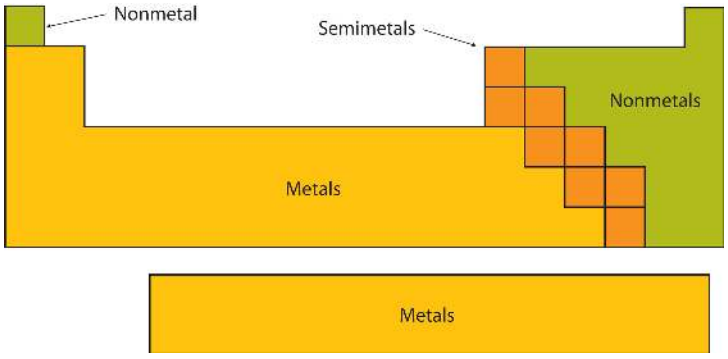


Figure 4.11.2: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

Example 4.11.1

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 4.11.1, 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 4.11.1

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 4.11.3. 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**.

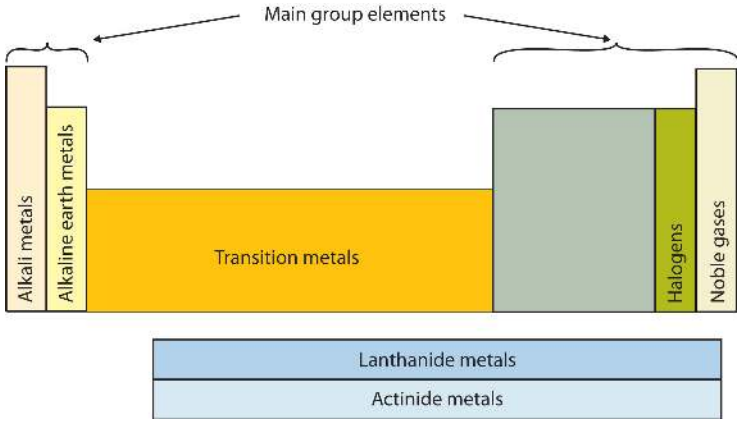


Figure 4.11.3: Special Names for Sections of the Periodic Table. (CC BY-NC-SA; Anonymous by request)

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 4.11.2: 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 4.11.2: 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 4.11.3: 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 4.11.3: 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).

References

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2. Sisler, Harry H. Electronic structure, properties, and the periodic law. New york; Reinhold publishing corporation, 1963.
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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4.12: 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.

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

The cation produced in this way, $\mathrm{Na^+}$, 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 4.12.1 is a graphical depiction of this process.

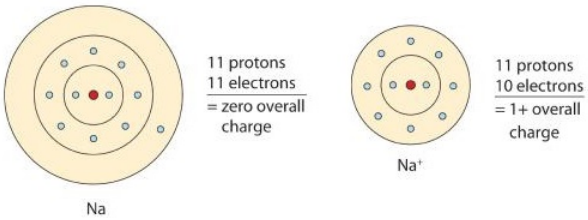


Figure 4.12.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge. Neutral sodium atom on left has 11 protons and 11 electrons. Sodium ion on right has 11 protons and 10 electrons, with a +1 overall charge.

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.)

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

In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, $\mathrm{Cl^-}$, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. Figure 4.12.2is a graphical depiction of this process.

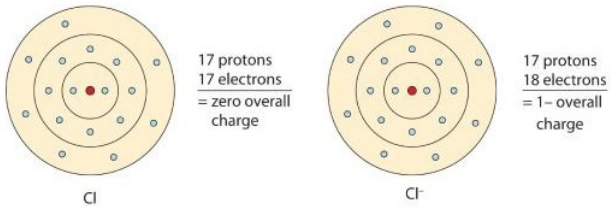


Figure 4.12.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge. Neutral chlorine atom on left has 17 protons and 17 electrons. Sodium ion on right has 17 protons and 18 electrons, with a -1 overall charge.

> *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 4.12.3 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}.

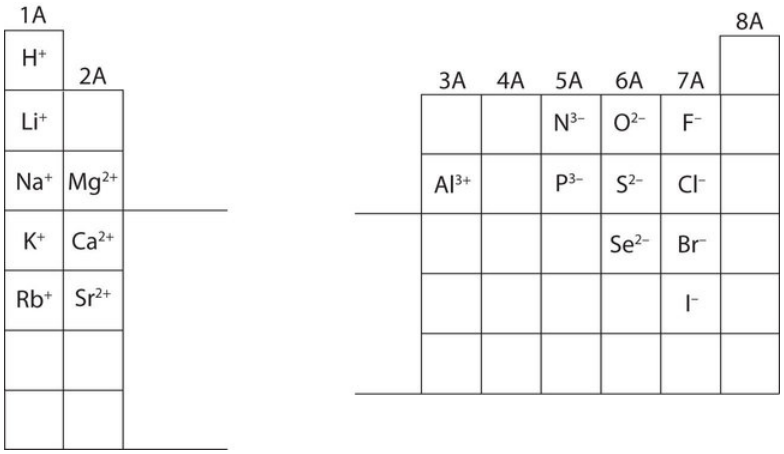


Figure 4.12.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

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CHAPTER OVERVIEW

5: Nomenclature of Molecules and Compounds

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: Writing Formulas for Ionic Compounds
5.3: Nomenclature- Naming Compounds
5.4: Naming Ionic Compounds
5.5: Naming Molecular Compounds
5.6: Naming Acids
5.7: Nomenclature Summary

5: Nomenclature of Molecules and Compounds is shared under a CK-12 license and was authored, remixed, and/or curated by Marisa Alviar-Agnew & Henry Agnew.

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.

$$2\,\mathrm{Na(s)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{NaCl(s)} \tag{5.1.1}$$

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.

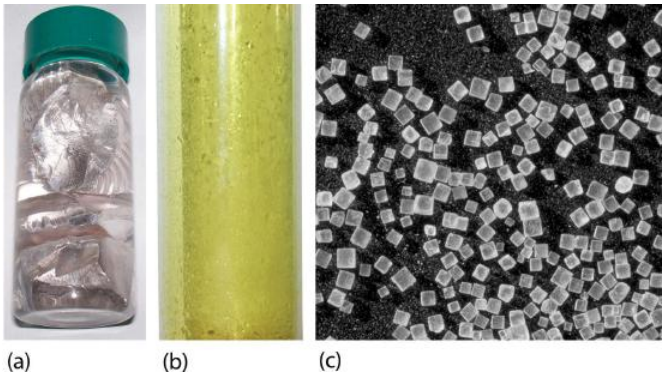


Figure 5.1.1: Sodium + Chlorine = Sodium Chloride (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride—salt—which is necessary for our survival. Source: Photo on the left courtesy of reenhorn1 and photo in the center courtesy 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.

$$\mathrm{C_{12}H_{22}O_{11}(s) + heat \rightarrow 12\,C(s) + 11\,H_2O(g)} \tag{5.1.2}$$



***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: 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 5.2.1: 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 5.2.2: 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-}

Crisscross Method	Write the formula for lead (IV) oxide
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 5.2.2

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 5.2.3: 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.	$Na^+ \quad S^{2-}$
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	This step is not necessary.
4. Write the final formula. Leave out all subscripts that are 1.	Na_2S

Exercise 5.2.3

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 5.2.1 lists the most common polyatomic ions.

Table 5.2.1: 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 5.2.4: 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 5.2.5

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 5.2.5

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 5.2.6

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 5.2.6

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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5.3: 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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5.4: 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 5.4.1: 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 5.4.1 lists the elements that use the common system, along with their respective cation names.

Table 5.4.2: Some Monatomic Anions

Ion	Name

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 5.4.2 lists the names of some common monatomic ions. The polyatomic ions have their own characteristic names, as discussed earlier.

Example 5.4.1

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 5.4.1

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 5.4.2

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 5.4.2

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

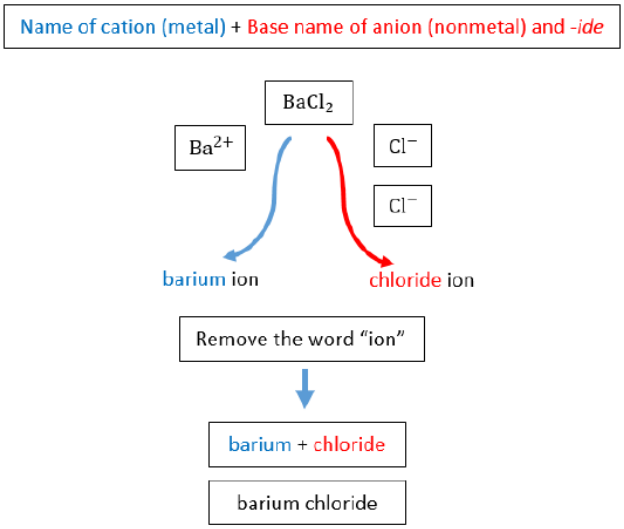


Figure 5.4.1: Naming $BaCl_2$
Naming formula: Name of metal cation + base
name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

Example 5.4.3: 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 5.4.3

Name each ionic compound.

a. AgI
b. MgO
c. Ca_3P_2

Answer a:

silver iodide

Answer b:

magnesium oxide

Answer c:

calcium phosphide

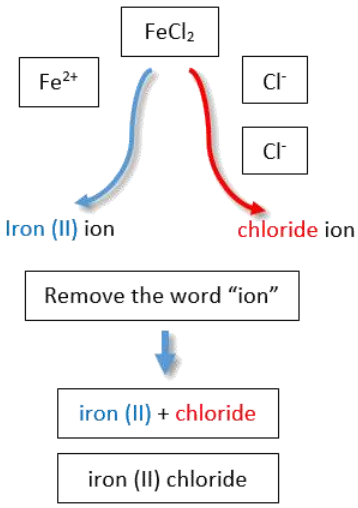
Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

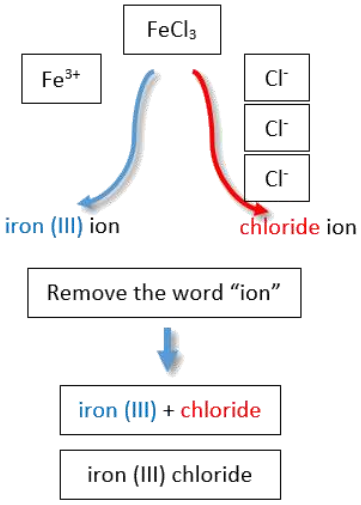
If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are 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 5.4.2).

Table 5.4.3: 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*

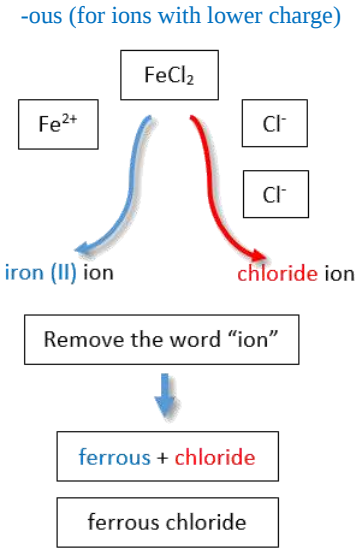


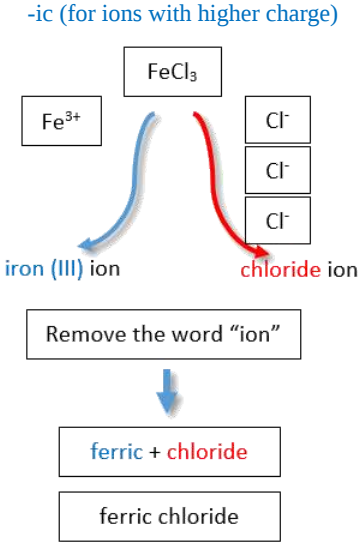


If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure 5.4.3) .

Table 5.4.4: 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 5.4.4:

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 5.4.4

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 5.4.6.

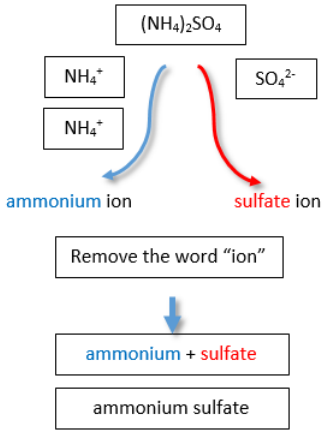


Figure 5.4.2: Naming Ionic Compounds with Polyatomic Ions

Example 5.4.5: 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 5.4.5A

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 5.4.1 is a synopsis of how to name simple ionic compounds.

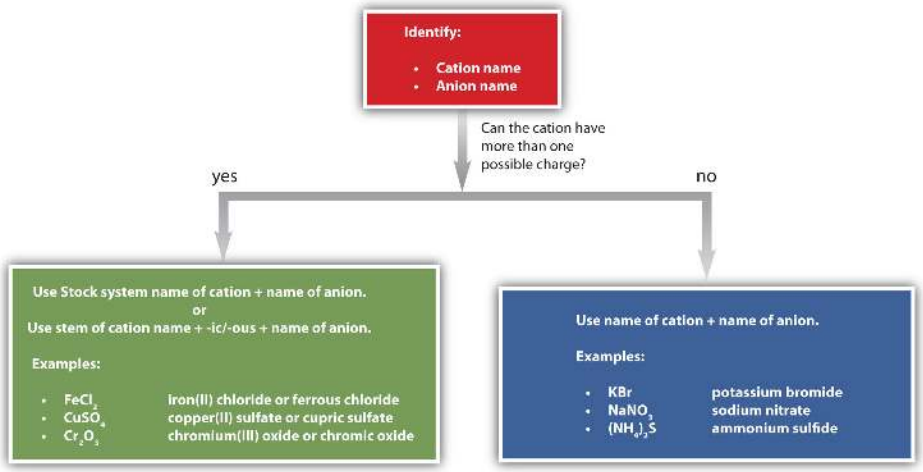


Figure 5.4.3: A Guide to Naming Simple Ionic Compounds.

? Exercise 5.4.5B

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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5.5: Naming Molecular Compounds

Learning Objectives

- Determine the name of a simple molecular compound from its chemical formula.

Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substances as water (H_2O) and carbon dioxide (CO_2). These compounds are very different from ionic compounds like sodium chloride ($NaCl$). Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **electrons** in such a way that a **bond** forms between a pair of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

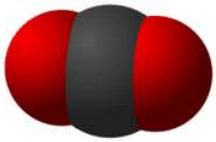


Figure 5.5.1: Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

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 5.5.2: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

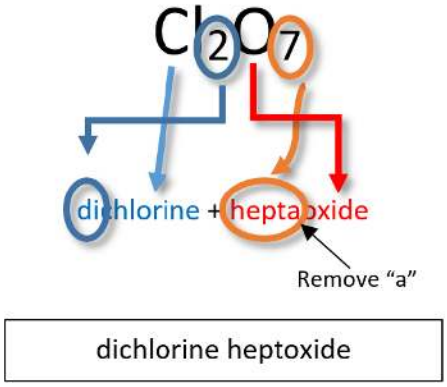
Naming *binary* (two-element) molecular compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 5.5.1 lists these numerical prefixes.

Table 5.5.1: 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-

Number of Atoms in Compound	Prefix on the Name of the Element
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 5.5.2.

Table 5.5.2

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 5.5.1

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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5.6: 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 $\left(H^+\right)$ when dissolved in water.



Figure 5.6.1: (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:

$$HCl \rightarrow H^+ + Cl^-$$

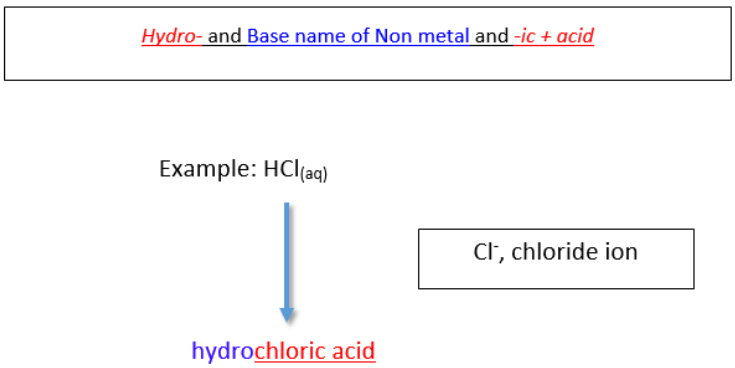
Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

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*.



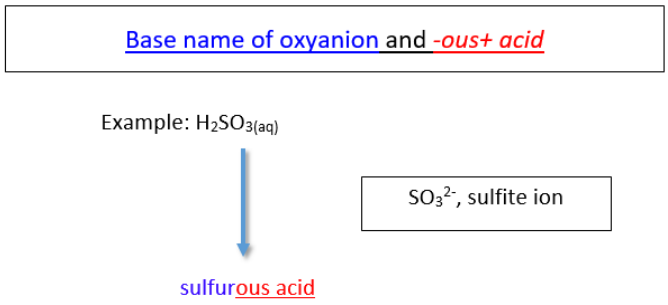
Formula for naming acids: Hydro- and Base name of nonmetal and -ic + acid. Example: HCl is hydrochloric acid.

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.

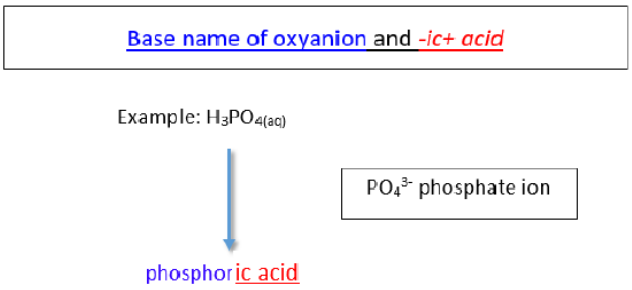
The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.



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.



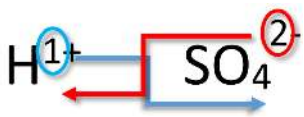
Formula for naming oxyanions with -ate ending: Base name of oxyanion and -ic + acid. Example: H3PO4 is phosphoric acid.

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 5.6.2: *Crisscross approach to writing formula for sulfuric acid.*

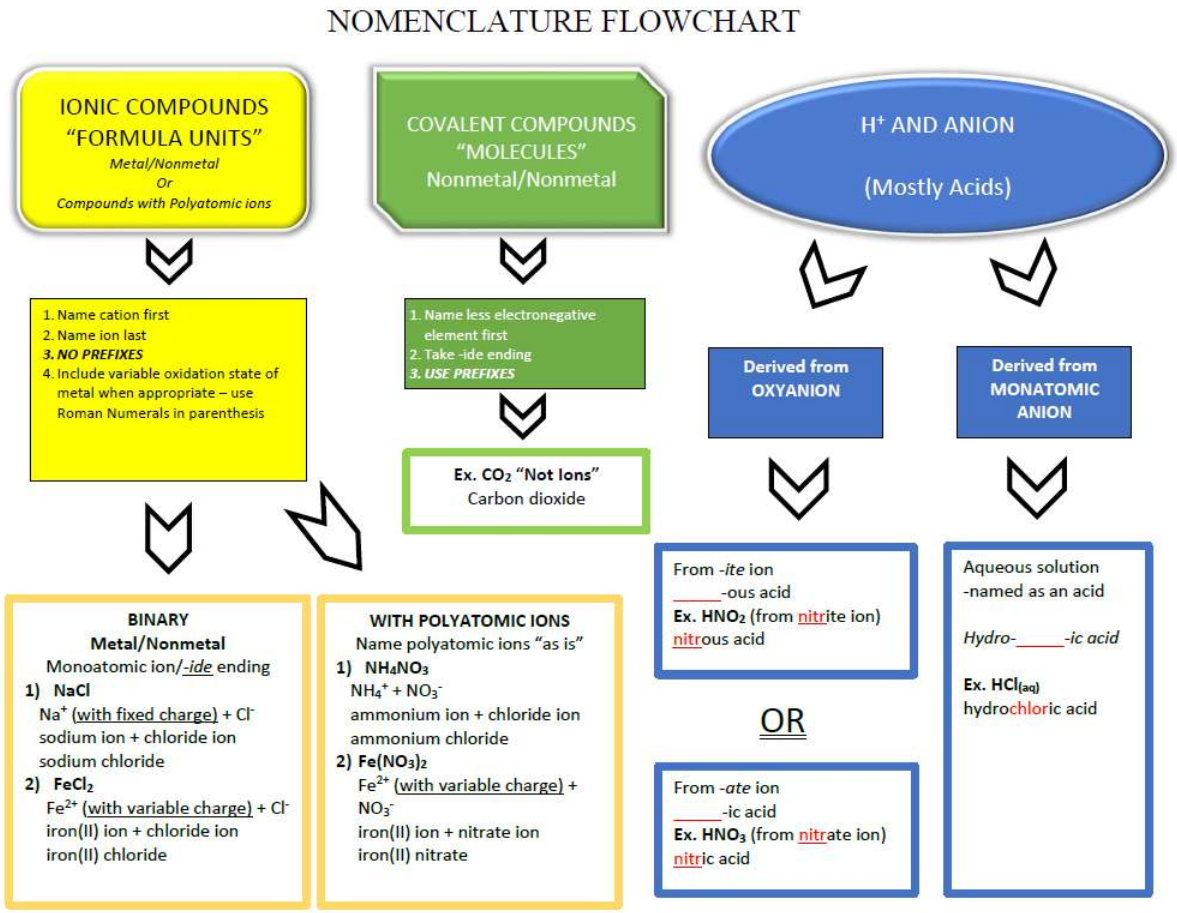
Summary

- 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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5.7: Nomenclature Summary



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CHAPTER OVERVIEW

6: Chemical Reactions

6.1: Evidence of a Chemical Reaction
6.2: The Chemical Equation
6.3: How to Write Balanced Chemical Equations
6.4: Energy and Chemical and Physical Change

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6.1: 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.

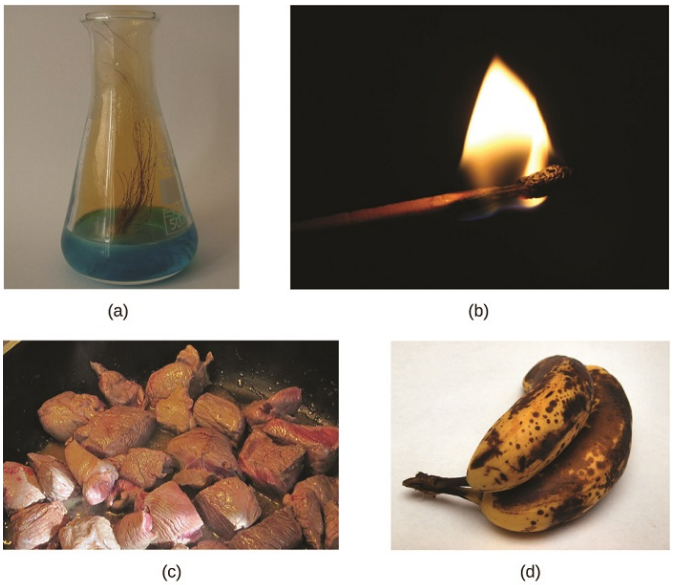


Figure 6.1.1: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes 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 6.1.1).



***Video*6.1.1*:** *Evidence of a Chemical Reaction*

Example 6.1.1: 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 6.1.1

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 6.1.2: 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 6.1.2

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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6.2: The Chemical Equation

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.

$$\underbrace{\text{Flour} + \text{Butter} + \text{Sugar} + \text{Vanilla} + \text{Baking Soda} + \text{Eggs} + \text{Chocolate Chips}}_{\text{Ingredients} = \text{Reactants}} \rightarrow \underbrace{\text{Cookies}}_{\text{Product}}$$

Writing Chemical Equations

When sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen, $\mathrm{SO_2} + \mathrm{O_2}$, are reactants and sulfur trioxide, $\mathrm{SO_3}$, is the product.

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

In chemical reactions, the reactants are found before the symbol "$\rightarrow$" and the products are found after the symbol "$\rightarrow$". The general equation for a reaction is:

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

There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. Table $6.2.1$ shows a listing of symbols used in chemical equations.

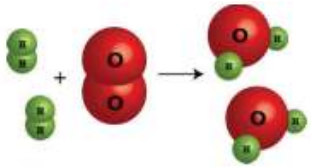
Table 6.2.1: Symbols Used in Chemical Equations

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

Symbol	Description	Symbol	Description
$\xrightarrow{\text{Pt}}$	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 6.2.1*: 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 6.2.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. $\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$
b. Gaseous propane, $\mathrm{C_3H_8}$, burns in oxygen gas to produce gaseous carbon dioxide and liquid water.
c. Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

Solution

a. An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

b. Reactants: propane ($\mathrm{C_3H_8}$) and oxygen ($\mathrm{O_2}$)

Product: carbon dioxide ($\mathrm{CO_2}$) and water ($\mathrm{H_2O}$)

$$\mathrm{C_3H_8}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

$$\mathrm{HF}\,(g) + \mathrm{K_2CO_3}\,(aq) \rightarrow \mathrm{KF}\,(aq) + \mathrm{H_2O}\,(l) + \mathrm{CO_2}\,(g)$$

Exercise 6.2.1

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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6.3: 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.

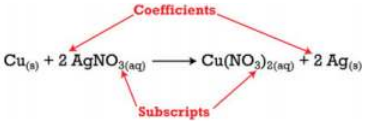
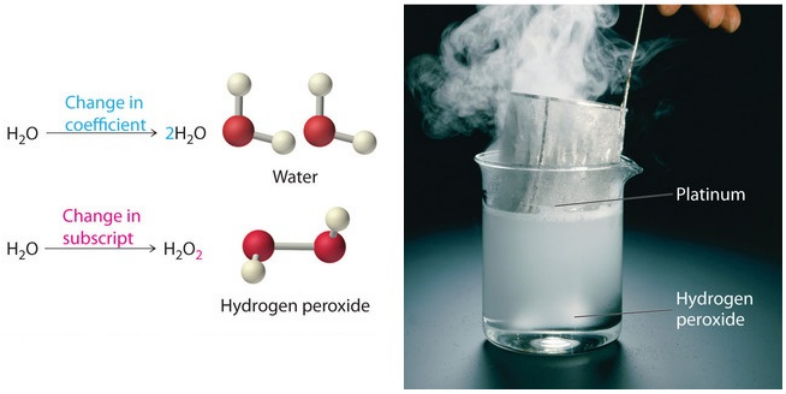


Figure 6.3.1: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (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 6.3.1.



Original molecule H_2O: if the coefficient 2 is added in front, that makes 2 water molecules; but if the subscript 2 is added to make 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 6.3.1: Combustion of Heptane

Balance the chemical equation for the combustion of Heptane (C_7H_{16}).

$$C_7H_{16}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Solution

Solutions to Example 6.3.1

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: $$C_7H_{16}(l) + O_2(g) \rightarrow \underline{7}CO_2(g) + H_2O(g)$$ • 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: $$C_7H_{16}(l) + O_2(g) \rightarrow 7\,CO_2(g) + \underline{8}H_2O(g)$$ • 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: $$C_7H_{16}(l) + \underline{11}O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g)$$ • 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 6.3.2: 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: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ • 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**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$

Steps	Example
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 6.3.3: 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. $\mathrm{Pb(NO_3)_2(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)}$
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. $\mathrm{Pb(NO_3)_2(aq) + \underline{2}NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)}$ • 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: $\mathrm{Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow \underline{2}NaNO_3(aq) + PbCl_2(s)}$ • 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.**	$\mathrm{Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow 2\,NaNO_3(aq) + PbCl_2(s)}$ • 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 6.3.1

Is each chemical equation balanced?

a. $2\,Hg(\ell) + O_2(g) \rightarrow Hg_2O_2(s)$
b. $C_2H_4(g) + 2\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(g)$
c. $Mg(NO_3)_2(s) + 2\,Li(s) \rightarrow Mg(s) + 2\,LiNO_3(s)$

Answer a

yes

Answer b

no

Answer c

yes

Exercise 6.3.2

Balance the following chemical equations.

a. $N_2(g) + O_2(g) \rightarrow NO_2(g)$
b. $Pb(NO_3)_2(aq) + FeCl_3(aq) \rightarrow Fe(NO_3)_3(aq) + PbCl_2(s)$
c. $C_6H_{14}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

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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6.4: 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.

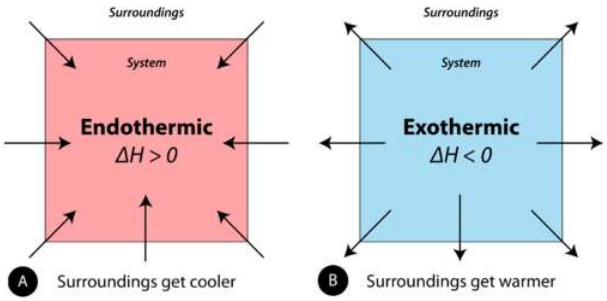


Figure 6.4.1: (A) Endothermic reaction. (B) Exothermic reaction.

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 6.4.1

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 6.4.1

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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CHAPTER OVERVIEW

7: Chemical Reactions in Aqueous Solutions

7.1: Aqueous Solutions and Solubility - Compounds Dissolved in Water
7.2: Precipitation Reactions
7.3: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations
7.4: Acid–Base and Gas Evolution Reactions
7.5: Oxidation–Reduction Reactions
7.6: Classifying Chemical Reactions

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7.1: Aqueous Solutions and Solubility - Compounds Dissolved in Water

Learning Objectives

- Define and give examples of electrolytes.

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called nonelectrolytes. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 7.1.1).

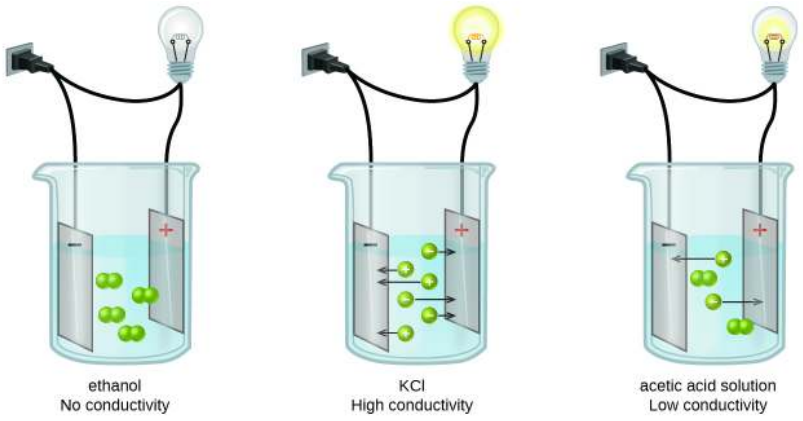


Figure 7.1.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram 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.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 7.1.2. 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.

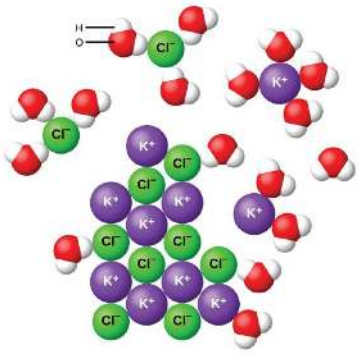


Figure 7.1.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight 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.

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure 7.1.2 shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system, as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Solubility Rules

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both products, sodium chloride and ammonium nitrate, are soluble and would remain in the solution as ions. Every ion is a spectator ion and there is no net ionic equation at all. It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (Tables 7.1.1 and 7.1.2).

Table 7.1.1: Solubility Rules for Soluble Substances

Soluble in Water	Important Exceptions (Insoluble)
All Group IA and NH_4^+ salts	none
All nitrates, chlorates, perchlorates and acetates	none
All sulfates	$CaSO_4$, $BaSO_4$, $SrSO_4$, $PbSO_4$
All chlorides, bromides, and iodides	AgX, Hg_2X_2, PbX_2 (X= Cl, Br, or I)

Table 7.1.2: Solubility Rules for Sparingly Soluble Substances

Sparingly Soluble in Water	Important Exceptions (Soluble)
All carbonates and phosphates	Group IA and NH_4^+ salts
All hydroxides	Group IA and NH_4^+ salts; Ba^{2+}, Sr^{2+}, Ca^{2+} sparingly soluble
All sulfides	Group IA, IIA and NH_4^+ salts; MgS, CaS, BaS sparingly soluble
All oxalates	Group IA and NH_4^+ salts
Special note: The following electrolytes are of only moderate solubility in water: CH_3COOAg, Ag_2SO_4, $KClO_4$. They will precipitate only if rather concentrated solutions are used.	

As an example on how to use the solubility rules, predict if a precipitate will form when solutions of cesium bromide and lead (II) nitrate are mixed.

$$Cs^+ (aq) + Br^- (aq) + Pb^{2+} (aq) + 2NO_3^- (aq) \rightarrow ?$$

The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table, cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds containing the bromide ion are soluble, but lead (II) is an exception. Therefore, the cesium and nitrate ions are spectator ions and the lead (II) bromide is a precipitate. The balanced net ionic reaction is:

$$Pb^{2+} (aq) + 2Br^- (aq) \rightarrow PbBr_2 (s)$$

Example 7.1.1: Solubility

Classify each compound as soluble or insoluble

a. $Zn(NO_3)_2$
b. $PbBr_2$
c. $Sr_3(PO_4)_2$

Solution

a. All nitrates are soluble in water, so $Zn(NO_3)_2$ is soluble.
b. All bromides are soluble in water, except those combined with Pb^{2+}, so $PbBr_2$ is insoluble.
c. All phosphates are insoluble, so $Sr_3(PO_4)_2$ is insoluble.

Exercise 7.1.1: Solubility

Classify each compound as soluble or insoluble.

a. $Mg(OH)_2$
b. KBr
c. $Pb(NO_3)_2$

Answer a

insoluble

Answer b

soluble

Answer c

soluble

Summary

Substances that dissolve in water to yield ions are called electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water. Solubility rules allow prediction of what products will be insoluble in water.

Contributions & Attributions

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7.2: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubility.

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. When a colorless solution of silver nitrate is mixed with a yellow-orange solution of potassium dichromate, a reddish precipitate of silver dichromate is produced.

$$\mathrm{AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq)} \tag{7.2.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD \rightarrow \underset{insoluble}{AD} + BC} \tag{7.2.2}$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called **double-displacement reactions**. Precipitation reactions are used to isolate metals that have been extracted from their ores, and to recover precious metals for recycling.



Video: Mixing potassium dichromate and silver nitrate together to initiate a precipitation reaction (Equation 7.2.1).

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of aqueous $NaCl$ solution is mixed with 500 mL of aqueous KBr solution, the final solution has a volume of 1.00 L and contains $\mathrm{Na^+(aq)}$, $\mathrm{Cl^-(aq)}$, $\mathrm{K^+(aq)}$, and $\mathrm{Br^-(aq)}$. As you will see in (Figure 7.2.1), none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other.

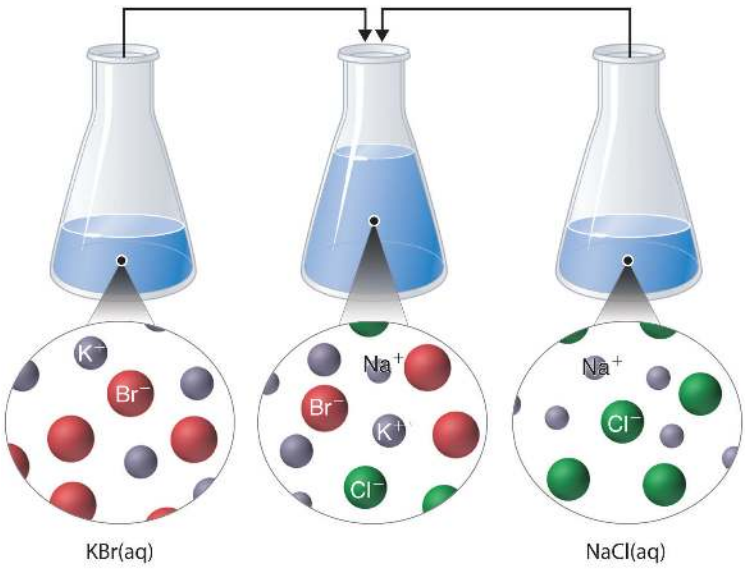


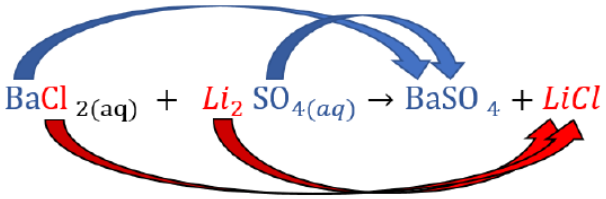
Figure 7.2.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Predicting Precipitation Reactions

A precipitation reaction occurs when a solid precipitate forms after mixing two strong electrolyte solutions. As stated previously, if none of the species in the solution reacts then no net reaction occurred.

Predict what will happen when aqueous solutions of barium chloride and lithium sulfate are mixed.

Change the partners of the anions and cations on the reactant side to form new compounds (products):



Chemical equation of the reactants barium chloride and lithium sulfate forming the products barium sulfate and lithium chloride.

Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+}, Cl^{-}, Li^{+}, and SO_4^{2-} ions. The only possible exchange reaction is to form $LiCl$ and $BaSO_4$.

Correct the formulas of the products based on the charges of the ions.

No need to correct the formula as both compounds already have their charges balanced.

$$BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4 + LiCl$$

Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.

$$BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + LiCl(aq)$$

Table 7.5.1 from the previous section shows that $LiCl$ is soluble in water, but $BaSO_4$ is not soluble in water.

Balance the equation:

$$BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,LiCl(aq)$$

Although soluble barium salts are toxic, $BaSO_4$ is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine $BaSO_4$ particles in water.



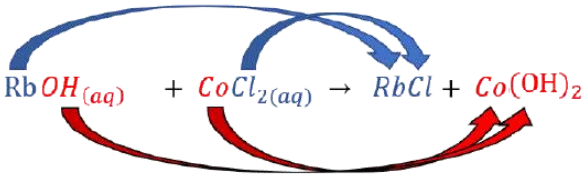
Figure 7.2.2: An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

Example 7.2.1

Predict what will happen if aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.

Solution

Solutions to Example 7.6.1

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	 Chemical equation of the reactants rubidium hydroxide and cobalt(II) chloride forming the products rubidium chloride and cobalt hydroxide.
Correct the formulas of the products based on the charges of the ions.	$\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl + Co(OH)_2}$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)}$
Balance the equation.	Coefficients already balanced. $\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)}$

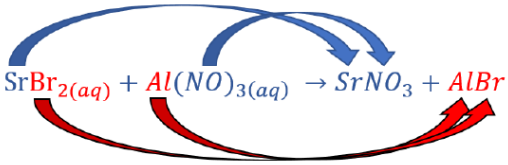
Example 7.2.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

Solution

Solutions for Example 7.6.2

Steps	Example

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	 Chemical equation of the reactants strontium bromide and aluminum nitrate forming the products strontium nitrate and aluminum bromide.
Correct the formulas of the products based on the charges of the ions.	$\mathrm{SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2 + AlBr_3}$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$\mathrm{SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2(aq) + AlBr_3(aq)}$ According to Table 7.5.1 from the previous section, both $\mathrm{AlBr_3}$ (rule 4) and $\mathrm{Sr(NO_3)_2}$ (rule 2) are soluble.
If all possible products are soluble, then no net reaction will occur.	$\mathrm{SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow}$ **NO REACTION**

Exercise 7.2.2

Using the information in Table 7.5.1 from the previous section, predict what will happen in each case involving strong electrolytes.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a

$Fe(OH)_2$ precipitate is formed.

Answer b

$Hg_3(PO_4)_2$ precipitate is formed.

Answer c

No Reaction.

Answer d

$CaCO_3$ is precipitate formed.

Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when two electrolyte solutions are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

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7.3: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The **complete chemical equation** can be written to describe what happens, and such an equation is useful in making chemical calculations.

$$\underbrace{\mathrm{BaCl_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\,NaCl(aq)}}_{\text{Complete Chemical Equation}} \tag{7.3.1}$$

However, Equation 7.3.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

$$\underbrace{\mathrm{Ba^{2+}(aq) + \overbrace{2\,Cl^-(aq)}^{\text{spectator}} + \overbrace{2\,Na^+(aq)}^{\text{spectator}} + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + \overbrace{2\,Na^+(aq)}^{\text{spectator}} + \overbrace{Cl^-(aq)}^{\text{spectator}}}}_{\text{Complete Ionic Equation}} \tag{7.3.2}$$

Equation 7.3.2 is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of $\mathrm{BaSO_4(s)}$ will form when *any* solution containing $\mathrm{Ba^{2+}(aq)}$ is mixed with *any* solution containing $\mathrm{SO_4^{2-}(aq)}$ (provided concentrations are not extremely small). This happens independently of the $\mathrm{Cl^-(aq)}$ and $\mathrm{Na^+(aq)}$ ions in Equation 7.3.2. These ions are called **spectator ions** because they do not participate in the reaction. When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $\mathrm{BaSO_4}$ the net ionic equation is

$$\underbrace{\mathrm{Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)}}_{\text{Net Ionic Equation}} \tag{7.3.3}$$

Example 7.3.1

a. When a solution of $\mathrm{AgNO_3}$ is added to a solution of $\mathrm{CaCl_2}$, insoluble AgCl precipitates. Write three equations (complete chemical equation, complete ionic equation, and net ionic equation) that describe this process.

b. Write the balanced net ionic equation to describe any reaction that occurs when the solutions of $\mathrm{Na_2SO_4}$ and $\mathrm{NH_4I}$ are mixed.

Solution

Solutions to Example 7.7.1

Equation Type	Example 7.3.1*a*	Example 7.3.1*b*
Complete Chemical Equation	$\mathrm{2\,AgNO_3(aq) + CaCl_2(aq) \longrightarrow 2\,AgCl(s) + Ca(NO_3)_2(aq)}$ The proper states and formulas of all products are written and the chemical equation is balanced.	$\mathrm{Na_2SO_4(aq) + 2\,NH_4I(aq) \longrightarrow 2\,NaI(aq) + (NH_4)_2SO_4(aq)}$ Both products are aqueous so there is no net ionic equation that can be written.
Complete Ionic Equation	$\mathrm{2\,Ag^+(aq) + 2\,NO_3^-(aq) + Ca^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow 2\,AgCl(s) + Ca^{2+}(aq) + 2\,NO_3^-(aq)}$ AgCl is a solid so it does not break up into ions in solution.	
Net Ionic Equation	$\mathrm{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}$ All spectator ions are removed. The chemical equation is written using the lowest common coefficients.	NaI and $\mathrm{(NH_4)_2SO_4}$ are both soluble. No net ionic equation. There is no reaction.

The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution. A $BaCl_2$ solution, for instance, is often used as a test for the presence of $SO_4^{2-}(aq)$ ions. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for $BaSO_4$. Thus, if $BaCl_2$ solution is added to an unknown solution which has previously been acidified, the occurrence of a white precipitate is proof of the presence of the SO_4^{2-} ion.



Figure 7.3.1: The three common silver halide precipitates: AgI, AgBr and AgCl (left to right). The silver halides precipitate out of solution, but often form suspensions before settling. (CC BY-SA 3.0; Cychr).

$AgNO_3$ solutions are often used in a similar way to test for halide ions. If $AgNO_3$ solution is added to an acidified unknown solution, a white precipitate indicates the presence of Cl^- ions, a cream-colored precipitate indicates the presence of Br^- ions, and a yellow precipitate indicates the presence of I^- ions (Figure 7.3.1). Further tests can then be made to see whether perhaps a mixture of these ions is present. When $AgNO_3$ is added to tap water, a white precipitate is almost always formed. The Cl^- ions in tap water usually come from the Cl_2 which is added to municipal water supplies to kill microorganisms.

? Exercise 7.3.1

Write balanced net ionic equations to describe any reaction that occurs when the following solutions are mixed.

a. $K_2CO_3 + SrCl_2$
b. $FeSO_4 + Ba(NO_3)_2$

Answer a

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow SrCO_3(s)$$

Answer b

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Ba(SO_4)(s)$$

Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

Contributions & Attributions

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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7.4: 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:

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$

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:

$$\mathrm{NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)} \tag{7.4.1}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$\mathrm{2\,NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\,H_2O(\ell)} \tag{7.4.2}$$

Example 7.4.1: 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) → $Ca(NO_3)_2$(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) + **2**HNO_3(aq) → $Ca(NO_3)_2$(aq) + **2**$H_2O(\ell)$
Additional step: identify the salt.		The salt formed is calcium nitrate.

Exercise 7.4.1

Hydrocyanic acid ($\mathrm{HCN(aq)}$) can be neutralized by potassium hydroxide ($\mathrm{KOH(aq)}$). 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 7.4.1):

$$\mathrm{2\,HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2\,NaNO_3(aq) + CO_2(g) + H_2O(l)}$$

Sulfuric acid reacts with calcium carbonate to form calcium sulfate, carbon dioxide, and water:

$$\mathrm{H_2SO_4(aq) + CaCO_3(aq) \rightarrow CaSO_4(aq) + CO_2(g) + H_2O(l)}$$

Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide, and water:

$$\mathrm{2\,HCl(aq) + CaCO_3(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)}$$

Figure 7.4.1 demonstrates this type of reaction:

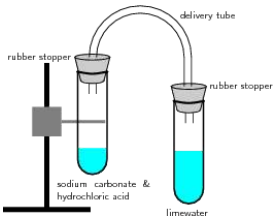


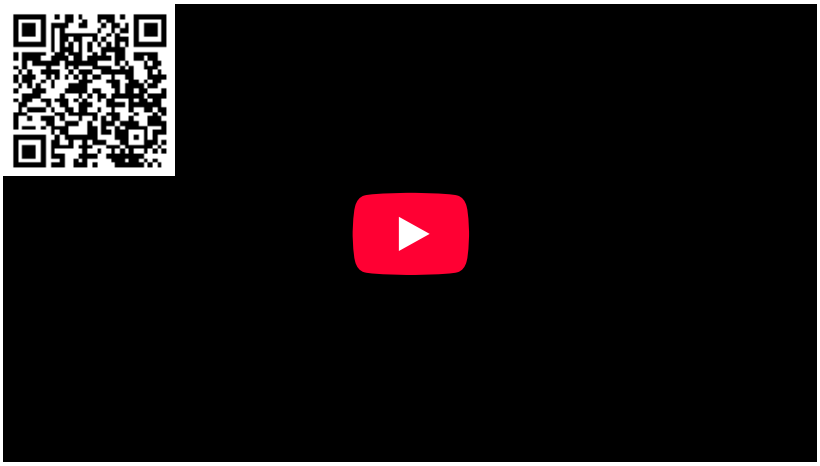
Figure 7.4.1: Reaction of acids with carbonates. In this reaction setup, lime water (water + calcium hydroxide) is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added 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 7.4.1: Types of Compounds That Undergo Gas-Evolution Reactions

Reactant Type	Intermediate Product	Gas Evolved	Example
sulfide	none	H_2S	$2\,HCl(aq) + K_2S \rightarrow H_2S(g) + 2\,KCl(a$
carbonates and bicarbonates	H_2CO_3	CO_2	$2\,HCl(aq) + K_2CO_2 \rightarrow H_2O(l) + CO_2$
sulfites and bisulfites	H_2SO_3	SO_2	$2\,HCl(aq) + K_2SO_2 \rightarrow H_2O(l) + SO_2($
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* 7.4.1:** *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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7.5: 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.

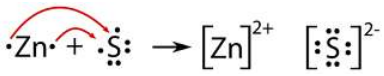


Figure 7.5.1: Reaction between zinc and sulfur.

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.

$$\underbrace{\mathrm{Zn} \rightarrow \mathrm{Zn_2^{2\,++}e^-}}_{\text{Oxidation}} \tag{7.5.1}$$

$$\underbrace{\mathrm{S^+2\,e^- \rightarrow S^{2\,-}}}_{\text{Reduction}} \tag{7.5.2}$$

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:

$$\mathrm{2\,Na^+Cl_2 \rightarrow 2\,NaCl} \tag{7.5.3}$$

The half reactions are as follows:

$$\underbrace{\mathrm{2\,Na \rightarrow 2\,Na^+ + 2\,e^-}}_{\text{Oxidation}} \tag{7.5.4}$$

$$\underbrace{\mathrm{Cl_2 + 2\,e^- \rightarrow 2\,Cl^-}}_{\text{Reduction}} \tag{7.5.5}$$

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 7.5.1: 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 7.5.1: 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 7.5.2: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

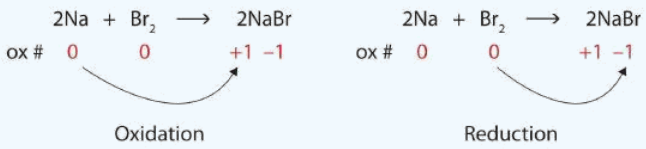
$$2\,\mathrm{Na} + \mathrm{Br_2} \rightarrow 2\,\mathrm{NaBr}$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the $\mathrm{Na^+}$ ions have an oxidation number of +1, while the $\mathrm{Br^-}$ ions have an oxidation number of −1.

$$\underset{0}{2Na} + \underset{0}{Br_2} \rightarrow \underset{+1-1}{2NaBr}$$

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 7.5.2: 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:

$$6H^+(aq) + 2\underset{+7}{MnO_4^-}(aq) + 5\underset{-1}{H_2O_2}(l) \rightarrow 2\underset{+2}{Mn^{2+}}(aq) + 5\underset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? 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 $\mathrm{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor.

$$2\mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{H_2O}\,(g) \tag{7.5.6}$$

Notice that this reaction also qualifies as a combination reaction.

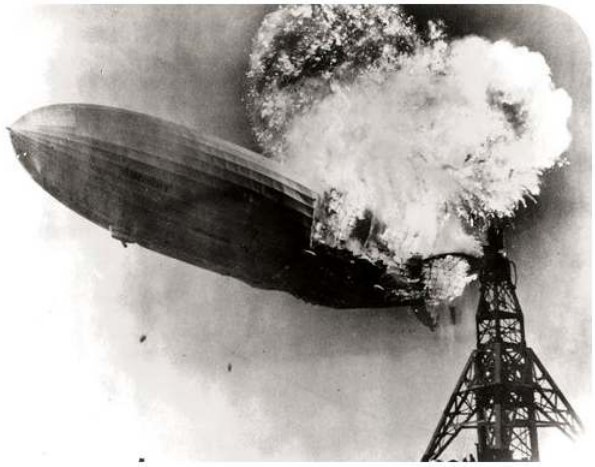


Figure 7.5.2: Explosion of the Hindenberg.

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 7.5.6).

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 $\left(C_3H_8\right)$ is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$C_3H_8\left(g\right)+5O_2\left(g\right)\rightarrow 3CO_2\left(g\right)+4H_2O\left(g\right)$$

Example 7.5.3: Combustion of Ethanol

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is 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.	$C_2H_5OH\left(l\right)+O_2\left(g\right)\rightarrow CO_2\left(g\right)+H_2O\left(g\right)$ 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.	$C_2H_5OH\left(l\right)+3O_2\left(g\right)\rightarrow 2CO_2\left(g\right)+3H_2O\left(g\right)$
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 7.5.3: Combustion of Hexane

Write the balanced equation for the combustion of hexane, C_6H_{14}

Answer

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

Contributors & Affiliations

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7.6: 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 7.6.1, 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 7.6.1: *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:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$2\mathrm{Na}\,(s) + \mathrm{Cl}_2\,(g) \rightarrow 2\mathrm{NaCl}\,(s)$$

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 (H_2, N_2, O_2, F_2, Cl_2, Br_2, and 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:

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

Sulfur reacts with oxygen to form sulfur dioxide:

$$\mathrm{S}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{SO_2}\,(g)$$

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:

$$2\mathrm{S}\,(s) + 3\mathrm{O_2}\,(g) \rightarrow 2\mathrm{SO_3}\,(g)$$

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:

$$2\mathrm{Fe}\,(s) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{FeO}\,(s)$$

$$4\mathrm{Fe}\,(s) + 3\mathrm{O_2}\,(g) \rightarrow 2\mathrm{Fe_2O_3}\,(s)$$

Example 7.6.1: 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 $\mathrm{K^+}$, while the oxide ion is $\mathrm{O^{2-}}$.
Solve.	The skeleton (unbalanced) equation: $$\mathrm{K}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{K_2O}\,(s)$$ The equation is then easily balanced with coefficients. $$4\mathrm{K}\,(s) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{K_2O}\,(s)$$
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:

$$2\mathrm{CO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{CO_2}\,(g)$$

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:

$$\mathrm{CaO}\,(s) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{Ca(OH)_2}\,(aq)$$

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.

$$\mathrm{SO_3}\,(g) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2SO_4}\,(aq)$$

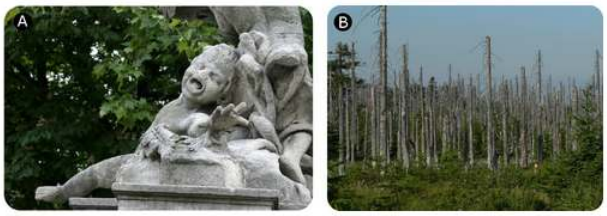


Figure 7.6.1: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

? Exercise 7.6.1

a. Write the chemical equation for the synthesis of silver bromide, AgBr.
b. Predict the products for the following reaction: $\mathrm{CO_2\,(g) + H_2O\,(l)}$

Answer a:

$$\mathrm{2Ag + Br_2 \rightarrow 2AgBr}$$

Answer b:

$$\mathrm{CO_2\,(g) + H_2O\,(l) \rightarrow H_2CO_3}$$

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:

$$\mathrm{AB \rightarrow A + B}$$

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:

$$\mathrm{2HgO\,(s) \rightarrow 2Hg\,(l) + O_2\,(g)}$$



***Video* 7.6.2:** *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:

$$\mathrm{CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)}$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water:

$$2\text{NaOH}\,(s) \rightarrow \text{Na}_2\text{O}\,(s) + \text{H}_2\text{O}\,(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water:

$$\text{H}_2\text{CO}_3\,(aq) \rightarrow \text{CO}_2\,(g) + \text{H}_2\text{O}\,(l)$$

Example 7.6.2: 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: $$\text{H}_2\text{O}\,(l) \overset{\text{elec}}{\rightarrow} \text{H}_2\,(g) + \text{O}_2\,(g)$$ Note the abbreviation "elec" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation. $$2\text{H}_2\text{O}\,(l) \overset{\text{elec}}{\rightarrow} 2\text{H}_2\,(g) + \text{O}_2\,(g)$$
Think about your result.	The products are elements and the equation is balanced.

Exercise 7.6.2

Write the chemical equation for the decomposition of:

a. Al_2O_3
b. Ag_2S

Answer a

$2\text{Al}_2\text{O}_3 \rightarrow 4\text{Al} + 3\text{O}_2$

Answer b

$\text{Ag}_2\text{S} \rightarrow 2\text{Ag} + \text{S}$

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:

$$\text{A} + \text{BC} \rightarrow \text{AC} + \text{B}$$

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:

$$\text{Y} + \text{XZ} \rightarrow \text{XY} + \text{Z}$$

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.

$$\mathrm{Mg}\,(s) + \mathrm{Cu(NO_3)_2}\,(aq) \rightarrow \mathrm{Mg(NO_3)_2}\,(aq) + \mathrm{Cu}\,(s)$$

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).

$$\mathrm{Zn}\,(s) + 2\mathrm{HCl}\,(aq) \rightarrow \mathrm{ZnCl_2}\,(aq) + \mathrm{H_2}\,(g)$$

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).

$$2\mathrm{Na}\,(s) + 2\mathrm{H_2O}\,(l) \rightarrow 2\mathrm{NaOH}\,(aq) + \mathrm{H_2}\,(g)$$



Figure 7.6.2: (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:

$$\mathrm{Cl_2}\,(g) + 2\mathrm{NaBr}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{Br_2}\,(l)$$

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 7.6.3

What are the products of the reaction between solid aluminum (Al) and iron (III) oxide ($\mathrm{Fe_2O_3}$)?

Solution

Solutions to Example 7.10.3

Steps	Example Solution

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 7.6.3

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:

$$2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow 2KNO_3\,(aq) + PbI_2\,(s) \qquad (7.6.1)$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (Figure 7.6.3). The other product of the reaction, potassium nitrate, remains soluble.



Figure 7.6.3: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation 7.6.1). (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 7.6.4

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 7.6.4

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:

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

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CHAPTER OVERVIEW

8: 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.

8.1: Prelude to Chemical Composition - How Much Sodium?
8.2: Counting Nails by the Pound
8.3: Counting Atoms by the Gram
8.4: Counting Molecules by the Gram
8.5: Chemical Formulas as Conversion Factors
8.6: Mass Percent Composition of Compounds
8.7: Mass Percent Composition from a Chemical Formula
8.8: Calculating Empirical Formulas for Compounds
8.9: Calculating Molecular Formulas for Compounds

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8.1: 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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8.2: 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 8.2.1). However, we can count them indirectly by using a common trick of "counting by weighing".

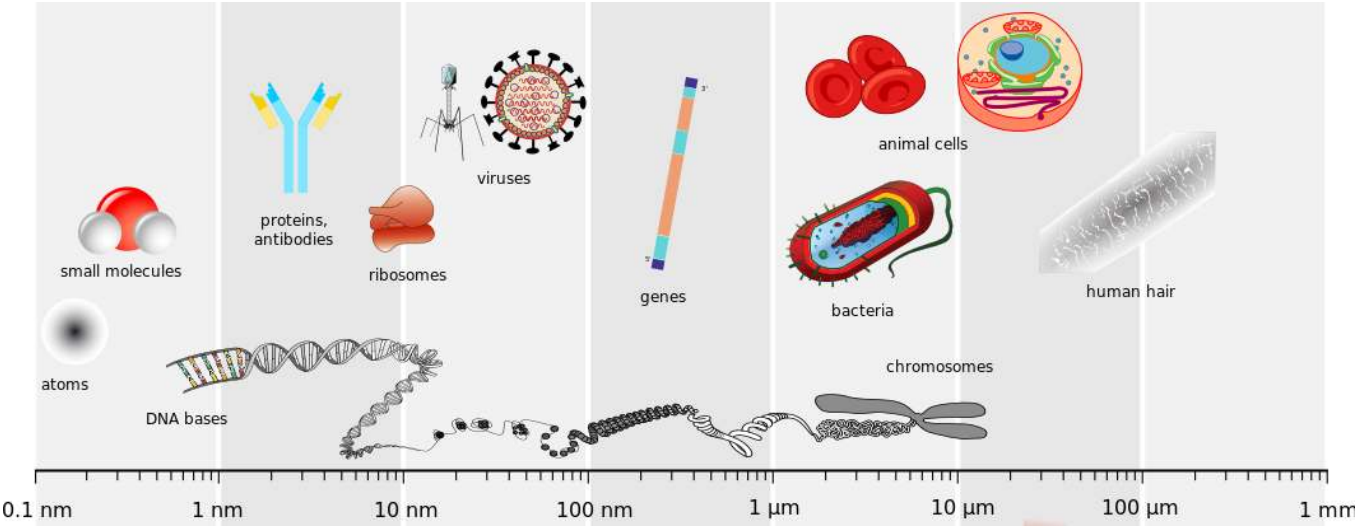


Figure 8.2.1: A comparison of the scales of various biological and technological objects. (CC BY-SA 3.0; Wikipedia)

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

$$\text{Number of big nails in box} = \frac{1227\,g}{0.450\,g/\text{big nail}} = 2,726.6\,\text{big nails} = 2,730\,\text{big nails}. \tag{8.2.1}$$

You have just counted the number of big nails in the box by weighing them (rather than by counting them individually).



Figure 8.2.2: 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 8.2.1:

$$\text{Number of small nails in box} = \frac{1227\,g}{0.230\,g/\text{small nail}} = 5,334.7\,\text{small nails} = 5,335\,\text{small nails}. \tag{8.2.2}$$

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 8.2.2, we can just use the conversion of how many nails are in a dozen:

$$\frac{5,335 \text{ small nails}}{12 \text{ small nails/dozen}} = 444.6 \text{ dozen small nails} \tag{8.2.3}$$

If we want to get this value from weighing, we use the "dozen mass" instead of individual mass:

$$12 \times 0.23g = 2.76\, g/\text{dozen small nails.} \tag{8.2.4}$$

So following Equation 8.2.2, we get:

$$\text{Number of dozens of small nails} = \frac{1227\, g}{2.76\, g/\text{dozen small nails}} = 444.6 \text{ dozen small nails} \tag{8.2.5}$$

and this is the same result as Equation 8.2.3. 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 8.2.1: 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 8.2.2: 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 8.2.3: 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 8.2.4: 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 8.2.1

What is the formula weight and molar mass for alum, $KAl(SO_4)_2 \bullet 12\,H_2O$?

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 8.2.1: Masses of each element in alum, $KAl(SO_4)_2 \bullet 12\,H_2O$

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 $KAl(SO_4)_2 \bullet 12\,H_2O$ = 474 grams alum $KAl(SO_4)_2 \bullet 12\,H_2O$

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8.3: 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 6.02×10^{23} particles and the name of this group is the **mole** (the abbreviation for ***mole*** is mol). One mole of any object is 6.02×10^{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 $6.02214076 \times 10^{23}$ particles, e.g., atoms, molecules, ions or electrons. The current definition was adopted in November 2018, revising its old definition based on the number of atoms in 12 grams of carbon-12 (^{12}C) (the isotope of carbon with relative atomic mass 12 Daltons, by definition). 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

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

Example 8.3.1: Moles of Carbon

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

Solution

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 molof carbon-12 atoms has a mass of 12.0 gand 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.

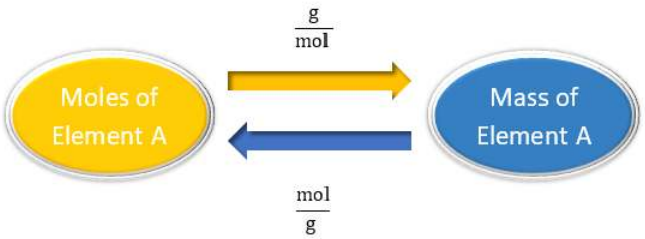


Figure 8.3.1: A Simple Flowchart for Converting Between Mass and Moles of an Element.
Flowchart: to convert moles of Element A to mass of Element A, use g/mol, and to convert vice versa, use mol/g.

Example 8.3.2: 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.	mol Cr → g Cr $\frac{52.00g\ Cr}{1\ mol\ Cr}$
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 8.3.3: 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.	g Si → mol Si $\frac{1\ mol\ Si}{28.09g\ Si}$
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 8.3.1

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 $6.02214076 \times 10^{23}$ 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=

Contributions & Attributions

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- Wikipedia

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8.4: 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 8.4.1.

EXAMPLE 8.4.1: ETHANOL

Calculate the molecular mass of ethanol, whose condensed structural formula is 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 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 8.4.1: FREON

Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, which has a condensed structural formula of CCl_3F. Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:

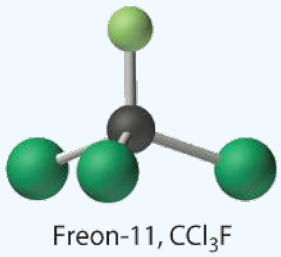


Figure 8.4.1: Molecular structure of freon-11, CCl_3F.

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 8.4.2: 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 8.4.2: 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 8.4.2: 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 8.4.1: 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 8.4.3.

EXAMPLE 8.4.3: CALCIUM CHLORIDE

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



Figure 8.4.3: 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 $CaCl_2$ Find: g $CaCl_2$
List other known quantities.	1 mol $CaCl_2$ = 110.98 g $CaCl_2$
Prepare a concept map and use the proper conversion factor.	mol $CaCl_2$ → g $CaCl_2$ $\frac{110.98\ g\ CaCl_2}{1\ mol\ CaCl_2}$
Cancel units and calculate.	$3.00\ \text{mol}\ CaCl_2 \times \frac{110.98\ \text{g}\ CaCl_2}{1\ \text{mol}\ CaCl_2} = 333\ \text{g}\ CaCl_2$
Think about your result.	

EXERCISE 8.4.3: CALCIUM OXIDE

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

Answer

420.60 g

EXAMPLE 8.4.4: 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 H_2O Find: mol H_2O
List other known quantities.	1 mol H_2O = 18.02 g H2O
Prepare a concept map and use the proper conversion factor.	g H_2O → mol H_2O $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$
Cancel units and calculate.	$108\ \text{g}\ H_2O \times \frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O} = 5.99\ \text{mol}\ H_2O$
Think about your result.	

EXERCISE 8.4.4: NITROGEN GAS

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

Answer

210 g

CONVERSIONS BETWEEN MASS AND NUMBER OF PARTICLES

In "Conversions Between Moles and Mass", you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to moles. To convert from mass to number of particles or vice-versa, it will first require a conversion to moles as shown in Figure 8.4.1 and Example 8.4.5.

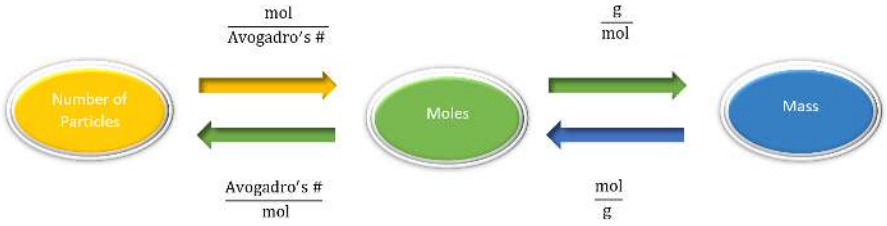


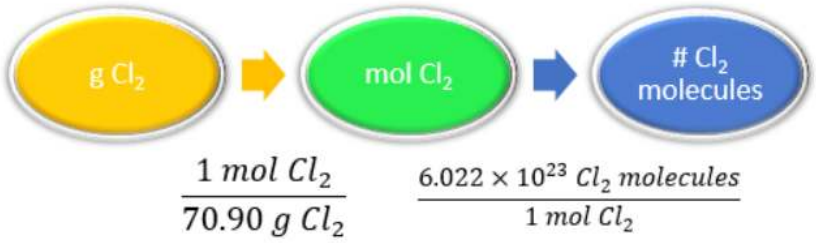
Figure 8.4.4: Conversion from number of particles to mass, or from mass to number of particles, requires two steps. To convert from number of particles to moles, use mol/Avogrado's #, an d to convert from moles to mass, use g/mol.

EXAMPLE 8.4.5: CHLORINE

How many molecules is 20.0 g of chlorine gas, 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 $6.022 \times 10^{2}3Cl_2$ molecules over 1 mole Cl_2.
Cancel units and calculate.	$20.0\ \text{g Cl}_2 \times \frac{1\ \text{mol Cl}_2}{70.90\ \text{g Cl}_2} \times \frac{6.02 \times 10^{23}\ \text{molecules Cl}_2}{1\ \text{mol Cl}_2}$ $= 1.70 \times 10^{23}\ \text{molecules Cl}_2$
Think about your result.	Since the given mass is less than half of the molar mass of chlorine, the resulting number of molecules is less than half of Avogadro's number.

? EXERCISE 8.4.5: 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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8.5: Chemical Formulas as Conversion Factors

Learning Objectives

- Use chemical formulas as conversion factors.

Figure 8.5.1 shows that we need 2 hydrogen atoms and 1 oxygen atom to make one water molecule. If we want to make two water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make five molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.

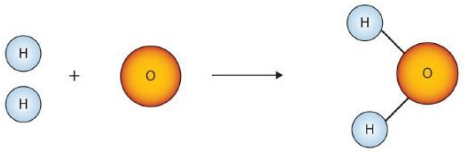


Figure 8.5.1 Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

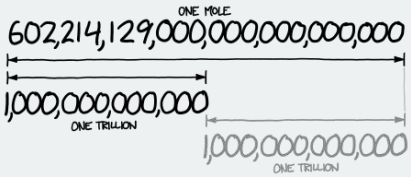
Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of water (H_2O) we can construct the relationships given in (Table 8.5.1).

Table 8.5.1: Molecular Relationships for Water

1 Molecule of H_2O Has	1 Mol of H_2O Has	Molecular Relationships
2 H atoms	2 mol of H atoms	$\frac{2\text{ mol H atoms}}{1\text{ mol }H_2O\text{ molecules}}$ or $\frac{1\text{ mol }H_2O\text{ molecules}}{2\text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1\text{ mol O atoms}}{1\text{ mol }H_2O\text{ molecules}}$ or $\frac{1\text{ mol }H_2O\text{ molecules}}{1\text{ mol O atoms}}$

The Mole is big

A mole represents a very large number! The number 602,214,129,000,000,000,000,000 looks about twice as long as a trillion, which means it's about a trillion trillion.



(CC BY-SA NC; what if? [what-if.xkcd.com]).

A trillion trillion kilograms is how much a planet weighs. If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Table 8.5.2: Molecular and Mass Relationships for Ethanol

1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular and Mass Relationships
2 C atoms	2 mol of C atoms	$\frac{2\text{ mol C atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{2\text{ mol C atoms}}$
6 H atoms	6 mol of H atoms	$\frac{6\text{ mol H atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{6\text{ mol H atoms}}$

1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular and Mass Relationships
1 O atom	1 mol of O atoms	$\frac{1\text{ mol O atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{1\text{ mol O atoms}}$
2 (12.01 amu) C 24.02 amu C	2 (12.01 g) C 24.02 g C	$\frac{24.02\text{ g C}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{24.02\text{ g C}}$
6 (1.008 amu) H 6.048 amu H	6 (1.008 g) H 6.048 g H	$\frac{6.048\text{ g H}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{6.048\text{ g H}}$
1 (16.00 amu) O 16.00 amu O	1 (16.00 g) O 16.00 g O	$\frac{16.00\text{ g O}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{16.00\text{ g O}}$

The following example illustrates how we can use the relationships in Table 8.5.2 as conversion factors.

Example 8.5.1: Ethanol

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms does it have?

Solution

Solutions to Example 6.5.1

Steps for Problem Solving	If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms does it have?
Identify the "given" information and what the problem is asking you to "find."	Given: 2.5 mol C_2H_6O Find: mol C atoms
List other known quantities.	1 mol C_2H_6O = 2 mol C
Prepare a concept map and use the proper conversion factor.	mol C_2H_6O → mol C atom $\frac{2\ mol\ C}{1\ mol\ C_2H_6O}$
Cancel units and calculate.	Note how the unit *mol C_2H_6O molecules* cancels algebraically. $2.5\ \text{mol }C_2H_6O\text{ molecules} \times \frac{2\text{ mol C atoms}}{1\ \text{mol }C_2H_6O\text{ molecules}} = 5.0\text{ mol C at}$
Think about your result.	There are twice as many C atoms in one C_2H_6O molecule, so the final amount should be double.

Exercise 8.5.1

If a sample contains 6.75 mol of Na_2SO_4, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

Answer

13.5 mol Na atoms, 6.75 mol S atoms, and 27.0 mol O atoms

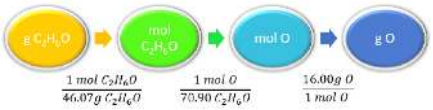
The fact that 1 mol equals 6.022×10^{23} items can also be used as a conversion factor.

Example 8.5.2: Oxygen Mass

Determine the mass of Oxygen in 75.0g of C_2H_6O.

Solution

Solutions to Example 6.5.2

Steps for Problem Solving	Determine the mass of Oxygen in 75.0g of C_2H_6O
Identify the "given" information and what the problem is asking you to "find."	Given: 75.0g C_2H_6O Find: g O
List other known quantities.	1 mol O = 16.0g O 1 mol C_2H_6O = 1 mol O 1 mol C_2H_6O = 46.07g C_2H_6O
Prepare a concept map and use the proper conversion factor.	 The conversion factors are 1 mol C2H6O over 46.07 g C2H6O, 1 mol O over 1 mol C2H6O, and 16.00 g O over 1 mole O.
Cancel units and calculate.	$75.0\ \cancel{\text{g } C_2H_6O} \times \frac{1\ \text{mol } \cancel{C_2H_6O}}{46.07\ \cancel{\text{g } C_2H_6O}} \times \frac{1\ \cancel{\text{mol O}}}{1\ \cancel{\text{mol } C_2H_6O}} \times \frac{16.00\ \text{g O}}{1\ \cancel{\text{mol O}}} = 26$
Think about your result.	

Exercise 8.5.2

a. How many molecules are present in 16.02 mol of C_4H_{10}? How many C atoms are in 16.02 mol?
b. How many moles of each type of atom are in 2.58 mol of Na_2SO_4?

Answer a:

9.647 x 10^{24} C_4H_{10} molecules and 3.859 x 10^{25} C atoms

Answer b:

5.16 mol Na atoms, 2.58 mol S atoms, and 10.3 mol O atoms

Summary

In any given formula, the ratio of the number of moles of molecules (or formula units) to the number of moles of atoms can be used as a conversion factor.

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8.6: 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 8.6.1: 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 gof 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 8.6.1

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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8.7: 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 8.7.1

Dichlorine heptoxide $\left(Cl_2O_7\right)$ 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 $\left(Cl_2O_7\right)$.**
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.	$$\%\text{Cl} = \frac{70.90\text{ g Cl}}{182.90\text{ g}} \times 100\% = 38.76\%\text{ Cl}$$ $$\%\text{ O} = \frac{112.00\text{ g O}}{182.90\text{ g}} \times 100\% = 61.24\%\text{ O}$$ Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%.
Think about your result.	The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is $38.76\%\text{ Cl}$ and $61.24\%\text{ O}$. Suppose that you needed to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element.

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

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

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

? Exercise 8.7.1

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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8.8: 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 8.8.1

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 $= \mathrm{Fe}_?\mathrm{O}_?$
Calculate	

Steps for Problem Solving	**Find the empirical formula of a compound of 69.94% iron and 30.06% oxygen.**
a. Assume a 100 g sample, convert the same % values to grams.	$69.94\ \text{g Fe}$ $30.06\ \text{g O}$
b. Convert to moles.	$69.94\ \text{g Fe} \times \frac{1\ \text{mol Fe}}{55.85\ \text{g Fe}} = 1.252\ \text{mol Fe}$ $30.06\ \text{g O} \times \frac{1\ \text{mol O}}{16.00\ \text{g O}} = 1.879\ \text{mol O}$
c. Divide both moles by the smallest of the results.	$\text{Fe}: \frac{1.252\ \text{mol}}{1.252}$ $\text{O}: \frac{1.879\ \text{mol}}{1.252}$ The "non-whole number" empirical formula of the compound is $\text{Fe}_1\text{O}_{1.5}$
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 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 8.8.1

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Answer

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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8.9: 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.

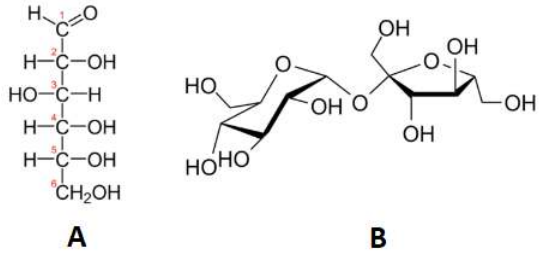


Figure 8.9.1: (A) the molecular structure of glucose and (B) the molecular structure of sucrose.

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).

$$n = \frac{MM(molarmass)}{EFM(empiricalformulamolarmass)}$$

Table 8.9.1 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 8.9.2. They are very different compounds, yet both have the same empirical formula of CH_2O.

Table 8.9.1: 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

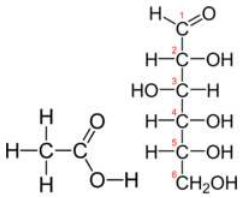


Figure 8.9.2: Acetic acid (left) has a molecular formula of $C_2H_4O_2$, while glucose (right) has a molecular formula of $C_6H_{12}O_6$. Both have the empirical formula CH_2O.

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 8.9.1

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 8.9.1

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

9: Quantities in Chemical Reactions

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.

9.1: Climate Change - Too Much Carbon Dioxide
9.2: Making Pancakes- Relationships Between Ingredients
9.3: Making Molecules- Mole-to-Mole Conversions
9.4: Making Molecules- Mass-to-Mass Conversions
9.5: Stoichiometry
9.6: Limiting Reactant and Theoretical Yield
9.7: Limiting Reactant, Theoretical Yield, and Percent Yield from Initial Masses of Reactants
9.8: Enthalpy Change is a Measure of the Heat Evolved or Absorbed

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9.1: 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 9.1.1 shows CO_2 levels during the last three glacial cycles, as reconstructed from ice cores.

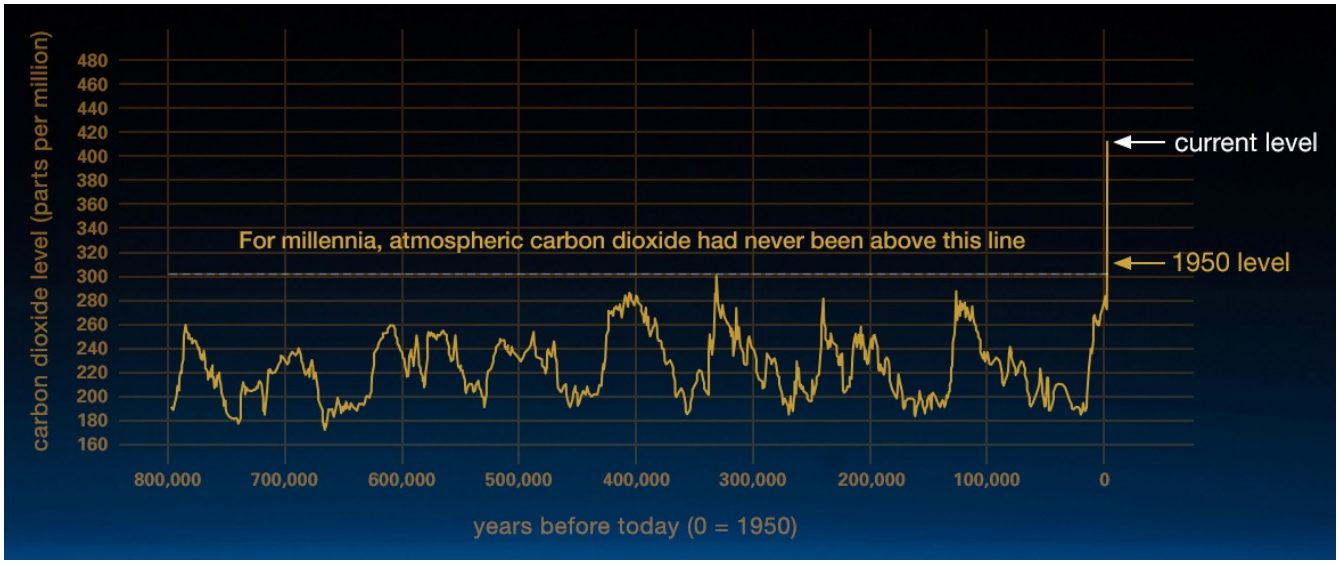


Figure 9.1.1: This graph, based on the comparison of atmospheric samples contained in ice cores and more recent direct measurements, provides evidence that atmospheric CO2 has increased since the Industrial Revolution. (Luthi, D., et al. 2008; Etheridge, D.M., et al. 2010; Vostok ice core data/J.R.R. 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:

$$2\,C_8H_{18}(l) + 21\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{9.1.1}$$

The balanced reaction in Equation 9.1.1 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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9.2: Making Pancakes- Relationships Between Ingredients

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9.3: MAKING MOLECULES- 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

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

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:

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

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

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

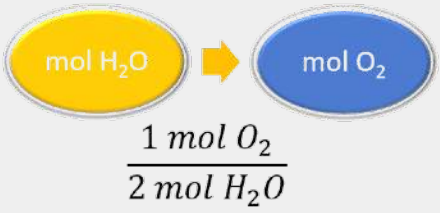
We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called *stoichiometry*.

EXAMPLE 9.3.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of $\mathrm{H_2O}$?

Solution

Solutions to Example 8.3.1

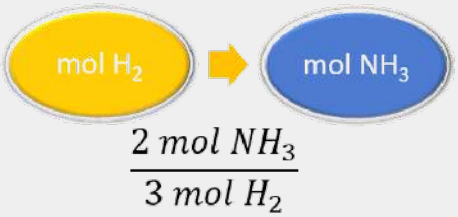
Steps for Problem Solving	How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?
Find a balanced equation that describes the reaction.	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{2}H_2 + O_2 \rightarrow \underline{2}H_2O$
Identify the "given" information and what 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.	$27.6\ \text{mol}\ \cancel{H_2O} \times \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ \cancel{H_2O}} = 13.8\ \text{mol}\ O_2$ To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.
Think about your result.	Since each mole of oxygen produces twice as many moles of water, it makes sense that the produced amount is greater than the reactant amount

EXAMPLE 9.3.2

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: $H_2 = 4.20$ mol Find: mol of NH_3
List other known quantities.	3 mol H_2 = 2 mol NH_3
Prepare a concept map and use the proper conversion factor.	 $\frac{2\ mol\ NH_3}{3\ mol\ H_2}$
Cancel units and calculate.	$4.20\ \text{mol}\ \cancel{H_2} \times \frac{2\ \text{mol}\ NH_3}{3\ \text{mol}\ \cancel{H_2}} = 2.80\ \text{mol}\ NH_3$ The reaction of 4.20 molof hydrogen with excess nitrogen produces 2.80 molof ammonia.
Think about your result.	The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

EXERCISE 9.3.3

a. Given the following balanced chemical equation:

$$C_5H_{12} + 8\,O_2 \rightarrow 5\,CO_2 + 6\,H_2O$$

, How many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

b. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react:

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

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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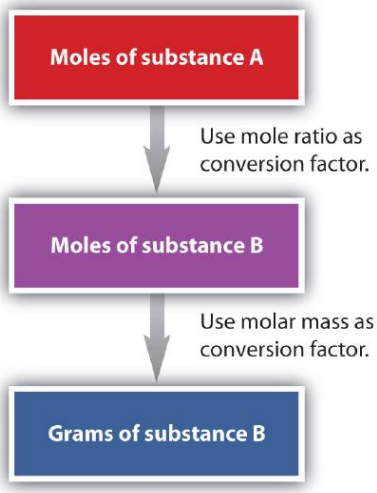
9.4: MAKING MOLECULES- MASS-TO-MASS CONVERSIONS

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

$$\mathrm{Fe_2O_3} + 3\,\mathrm{SO_3} \rightarrow \mathrm{Fe_2(SO_4)_3} \tag{9.4.1}$$

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:

$$3.59\ \text{mol}\ \cancel{\mathrm{Fe_2O_3}} \times \left(\frac{3\ \text{mol}\ \mathrm{SO_3}}{1\ \text{mol}\ \cancel{\mathrm{Fe_2O_3}}}\right) = 10.77\ \text{mol}\ \mathrm{SO_3} \tag{9.4.2}$$

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:

$$10.77\ \cancel{\text{mol}\ \mathrm{SO_3}} \times \left(\frac{80.06\ \text{g}\ \mathrm{SO_3}}{1\ \cancel{\text{mol}\ \mathrm{SO_3}}}\right) = 862\ \text{g}\ \mathrm{SO_3} \tag{9.4.3}$$

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.

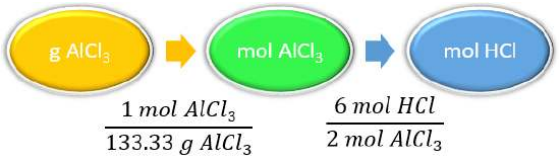
EXAMPLE 9.4.1: GENERATION OF ALUMINUM OXIDE

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

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

Solution

Solutions to Example 8.5.1

Steps for Problem Solving	Example 9.4.1
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 9.4.1: GENERATION OF ALUMINUM OXIDE

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

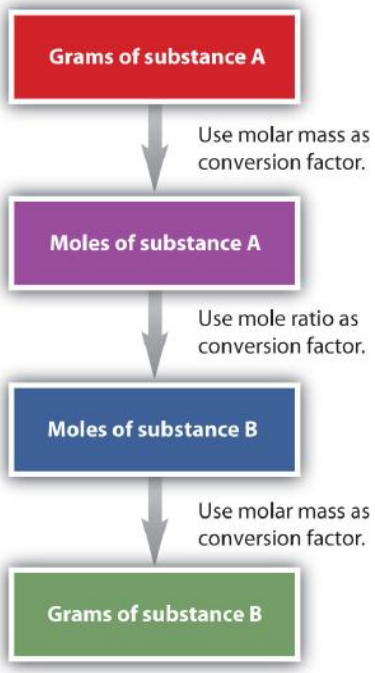
$$2\,AlCl_3 + 3\,H_2O(\ell) \rightarrow Al_2O_3 + 6\,HCl(g)$$

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

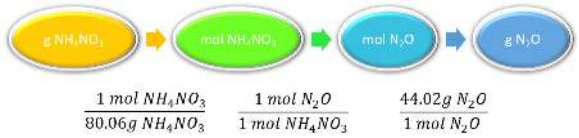
✔ EXAMPLE 9.4.2: DECOMPOSITION OF AMMONIUM NITRATE

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 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 9.4.2
Identify the "given" information and what the problem is asking you to "find."	Given: 45.7 g NH_4NO_3 Find: Mass N_2O =? g Mass H_2O =? g
List other known quantities.	1 mol NH_4NO_3 = 80.06 g 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.	 $\frac{1\ mol\ NH_4NO_3}{80.06g\ NH_4NO_3}$ $\frac{1\ mol\ N_2O}{1\ mol\ NH_4NO_3}$ $\frac{44.02g\ N_2O}{1\ mol\ N_2O}$ 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  $\frac{1\ mol\ NH_4NO_3}{80.06g\ NH_4NO_3}$ $\frac{2\ mol\ H_2O}{1\ mol\ NH_4NO_3}$ $\frac{18.02g\ H_2O}{1\ mol\ H_2O}$ 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 9.4.2: CARBON TETRACHLORIDE

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4(g) + 4\,Cl_2(g) \rightarrow CCl_2(l) + 4\,HCl(l)$$

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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9.5: 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: $\sigma\tau o\iota\kappa\eta\iota o\nu$, 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.

$$2\mathrm{CuSO_4} + 4\mathrm{KI} \rightarrow 2\mathrm{CuI} + 2\mathrm{K_2SO_4} + \mathrm{I_2}$$

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 ($\mathrm{CuSO_4}$) 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 $\left(\mathrm{NH_3}\right)$ from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

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

The balanced equation can be analyzed in several ways, as shown in the figure below.

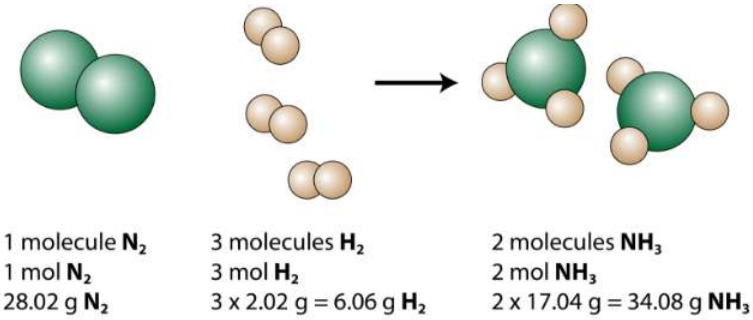


Figure 9.5.1: This representation of the production of ammonia from nitrogen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

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 mol of nitrogen has a mass of 28.02 g while 3 mol of hydrogen has a mass of 6.06 g and 2 mol of ammonia has a mass of 34.08 g

$$28.02 \text{ g } N_2 + 6.06 \text{ g } H_2 \rightarrow 34.08 \text{ g } NH_3$$

Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.

Example 9.5.1

The equation for the combustion of ethane (C_2H_6) is

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

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 9.5.1

For the following equation below, indicate the number of formula units or molecules, and the number of moles present in the balanced equation.

$$KBrO_3 + 6KI + 6HBr \rightarrow 7KBr + 3H_2O$$

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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9.6: 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:

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{9.6.1}$$

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.

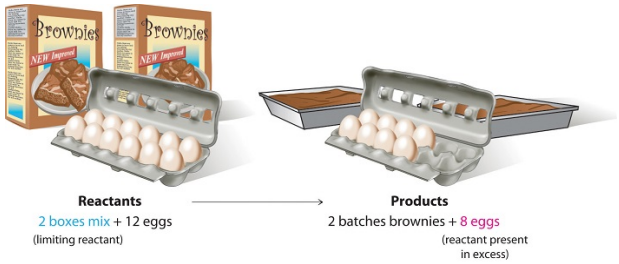


Figure 9.6.1: The Concept of a Limiting Reactant in the Preparation of Brownies. For a chemist, the **balanced** chemical equation is the recipe that must be followed. 2 boxes of brownie mix and 12 eggs results in 2 batches of brownies and 8 eggs; in this case the 8 eggs are reactant present in excess

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:

$$\text{H}_2 + \text{Cl}_2(g) \rightarrow 2\,\text{HCl}(g)$$

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 9.6.2).

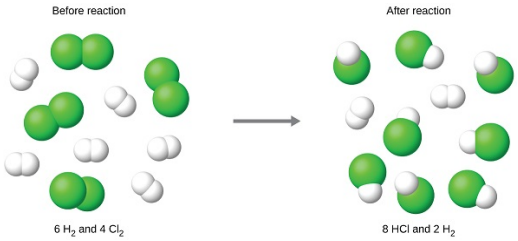


Figure 9.6.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. The figure shows a space-filling molecular 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 9.6.1: 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

$$4\ \text{mol } C_2H_3Br_3 \text{ to } 11\ \text{mol } O_2 \text{ to } 6\ \text{mol } H_2O \text{ to } 6\ \text{mol Br}$$

Step 2: Convert all given information into moles.

$$76.4\ \text{g } C_2H_3Br_3 \times \frac{1\ \text{mol } C_2H_3Br_3}{266.72\ \text{g } C_2H_3Br_3} = 0.286\ \text{mol } C_2H_3Br_3$$

$$49.1\ \text{g } O_2 \times \frac{1\ \text{mol } O_2}{32.00\ \text{g } O_2} = 1.53\ \text{mol } O_2$$

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,

$$1.53\ \text{mol } O_2 \times \frac{4\ \text{mol } C_2H_3Br_3}{11\ \text{mol } O_2} = 0.556\ \text{mol } C_2H_3Br_3 \text{ are required.}$$

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

$$4 \text{ mol } C_2H_3Br_3 \text{ to } 11 \text{ mol } O_2 \text{ to } 6 \text{ mol } H_2O \text{ to } 6 \text{ mol } Br_2$$

Step 2 and Step 3: Convert mass to moles and stoichiometry.

$$76.4 \text{ g } C_2H_3Br_3 \times \frac{1 \text{ mol } C_2H_3Br_3}{266.72 \text{ g } C_2H_3Br_3} \times \frac{8 \text{ mol } CO_2}{4 \text{ mol } C_2H_3Br_3} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 25.2 \text{ g } CO_2$$

$$49.1 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{8 \text{ mol } CO_2}{11 \text{ mol } O_2} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 49.1 \text{ g } CO_2$$

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 9.6.2: 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.

$$\underline{2} \text{ Mg (s)} + O_2 \text{ (g)} \rightarrow \underline{2} \text{ MgO (s)}$$

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.

$$2.40 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{2 \text{ mol MgO}}{2 \text{ mol Mg}} \times \frac{40.31 \text{ g MgO}}{1 \text{ mol MgO}} = 3.98 \text{ g MgO}$$

$$10.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{2 \text{ mol MgO}}{1 \text{ mol } O_2} \times \frac{40.31 \text{ g MgO}}{1 \text{ mol MgO}} = 25.2 \text{ g MgO}$$

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:

$$2.40 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{1 \text{ mol } O_2}{2 \text{ mol Mg}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 1.58 \text{ g } O_2$$

OR
Mass of excess reactant calculated using the mass of the product:

$$3.98 \text{ g MgO} \times \frac{1 \text{ mol MgO}}{40.31 \text{ g MgO}} \times \frac{1 \text{ mol } O_2}{2 \text{ mol MgO}} \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 1.58 \text{ g } O_2$$

Mass of total excess reactant given – mass of excess reactant consumed in the reaction:

$$10.0\text{g } O_2 \text{ - (available) } 1.58\text{g } O_2 \text{ (used)} = 8.42\text{g } O_2 \text{ (excess)}$$

Therefore, O_2 is in excess.

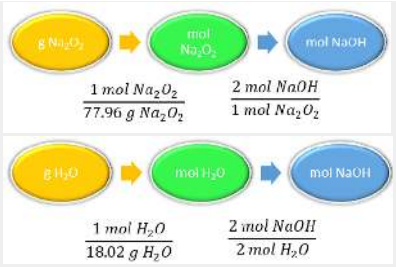
EXAMPLE 9.6.3: LIMITING REACTANT

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

$$Na_2O_2(s) + H_2O(l) \rightarrow NaOH(aq) + H_2O_2(l)$$

Solution

Solutions to Example 8.4.3

Steps for Problem Solving- The Product Method	Example 9.6.1
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) + **2**H_2O (l) → **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.	$78.0\ \text{g Na}_2\text{O}_2 \times \frac{1\ \text{mol Na}_2\text{O}_2}{77.96\ \text{g Na}_2\text{O}_2} \times \frac{2\ \text{mol NaOH}}{1\ \text{mol Na}_2\text{O}_2} \times \frac{40\ \text{g NaOH}}{1\ \text{mol NaOH}} = 2.00\ \text{mol NaOH}$ $29.4\ \text{g H}_2\text{O} \times \frac{1\ \text{mol H}_2\text{O}}{18.02\ \text{g H}_2\text{O}} \times \frac{2\ \text{mol NaOH}}{2\ \text{mol Na}_2\text{O}_2} \times \frac{40\ \text{g NaOH}}{1\ \text{mol NaOH}} = 1.63\ \text{mol NaOH}$ Therefore, H_2O is the *limiting reactant*.

Think about your result.

EXAMPLE 9.6.4: LIMITING REACTANT AND MASS OF EXCESS REACTANT

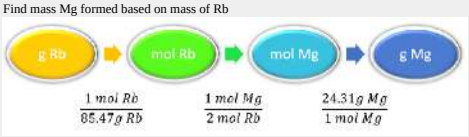
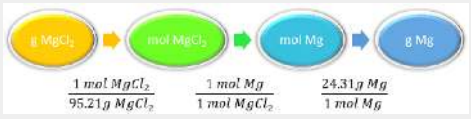
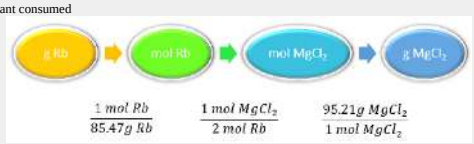
A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

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 9.6.2
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 9.6.1

Given the initial amounts listed, what is the limiting reactant, and what is the mass of the leftover reactant?

$$\underbrace{22.7\ g}_{MgO(s)} + \underbrace{17.9\ g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

Answer

H_2S is the limiting reagent; 1.5 g of MgO are left over.

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9.7: 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 $9.7.1$ illustrates the steps for determining percent yield.

EXAMPLE $9.7.1$: DECOMPOSITION OF POTASSIUM CHLORATE

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below:

$$2\text{KClO}_3\,(s) \rightarrow 2\text{KCl}\,(s) + 3\text{O}_2\,(g)$$

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 $\text{KClO}_3 = 40.0\text{ g}$

Mass of O_2 collected = 14.9g

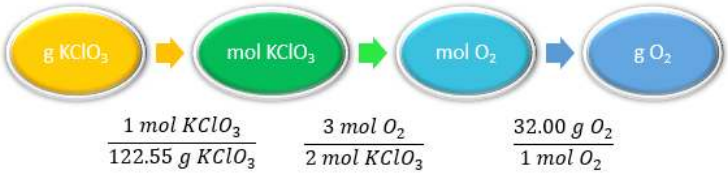
Find: Theoretical yield, g O_2

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 9.7.2: OXIDATION OF ZINC

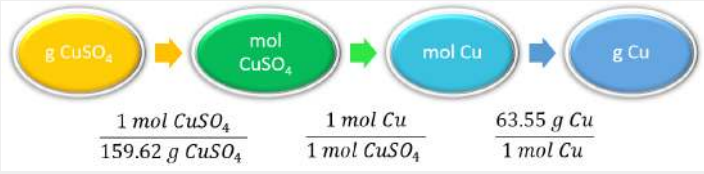
Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$\text{CuSO}_4(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{ZnSO}_4(aq)$$

What is the percent yield?

Solution

Solutions to Example 8.6.2

Steps for Problem Solving-The Product Method	Example 9.7.1
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.	$$1.274\ \text{g}\ \cancel{\text{CuSO}_4} \times \frac{1\ \text{mol}\ \cancel{\text{CuSO}_4}}{159.62\ \text{g}\ \cancel{\text{CuSO}_4}} \times \frac{1\ \text{mol}\ \cancel{\text{Cu}}}{1\ \text{mol}\ \cancel{\text{CuSO}_4}} \times \frac{63.55\ \text{g Cu}}{1\ \text{mol}\ \cancel{\text{Cu}}} = 0.5072\ \text{g Cu}$$ Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be: $$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$ $$= \left(\frac{0.392\ g\ \text{Cu}}{0.5072\ g\ \text{Cu}}\right) \times 100$$ $$= 77.3\%$$
Think about your result.	Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.

? EXERCISE 9.7.1

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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9.8: Enthalpy Change is a Measure of the Heat Evolved or Absorbed

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** 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 is 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.

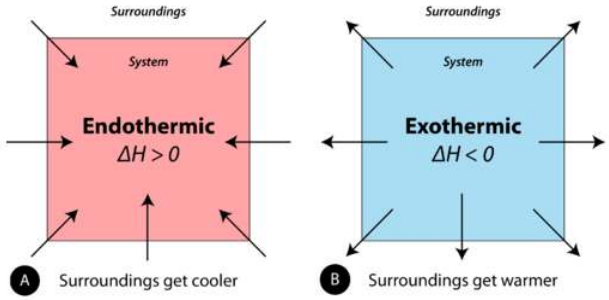


Figure 9.8.1: (A) Endothermic reaction. (B) Exothermic reaction.

Enthalpy

Heat changes in chemical reactions are often measured in the laboratory under conditions in which the reacting system is open to the atmosphere. In that case, the system is at a constant pressure. **Enthalpy** $(\boldsymbol{H})$ is the heat content of a system at constant pressure. Chemists routinely measure changes in enthalpy of chemical systems as reactants are converted into products. The heat that is absorbed or released by a reaction at constant pressure is the same as the enthalpy change, and is given the symbol ΔH. Unless otherwise specified, all reactions in this material are assumed to take place at constant pressure.

The change in enthalpy of a reaction is a measure of the differences in enthalpy of the reactants and products. The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds. Energy needs to be put into the system in order to break chemical bonds, as they do not come apart spontaneously in most cases. Bond formation to produce products will involve release of energy. The change in enthalpy shows the trade-offs made in these two processes. Does it take more energy to break bonds than that needed to form bonds? If so, the reaction is endothermic and the enthalpy change is positive. If more energy is produced in bond formation than that needed for bond breaking, the reaction is exothermic and the enthalpy is negative.

Several factors influence the enthalpy of a system. Enthalpy is an extensive property, determined in part by the amount of material we work with. The state of reactants and products (solid, liquid, or gas) influences the enthalpy value for a system. The direction of the reaction affects the enthalpy value. A reaction that takes place in the opposite direction has the same numerical enthalpy value, but the opposite sign.

Thermochemical Equation

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) + 890.4\ \mathrm{kJ}$$

The equation tells us that 1 mol of methane combines with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water. In the process, 890.4 kJ is released and so it is written as a product of the reaction. A **thermochemical equation** is a chemical equation that includes the enthalpy change of the reaction. The process in the above thermochemical equation can be shown visually in Figure 9.8.2.

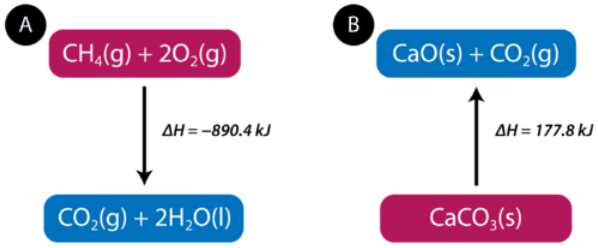


Figure 9.8.2: (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive.

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is -890.4 kJ. The thermochemical reaction can also be written in this way:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) \quad \Delta H = -890.4\ \mathrm{kJ}$$

Heats of reaction are typically measured in kilojoules. It is important to include the physical states of the reactants and products in a thermochemical equation as the value of the ΔH depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. The process is shown visually in Figure 9.8.2*B*. The thermochemical reaction is shown below.

$$\mathrm{CaCO_3}\,(s) + 177.8\ \mathrm{kJ} \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g)$$

Because the heat is absorbed by the system, the 177.8 kJ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \quad \Delta H = 177.8\ \mathrm{kJ}$$

The way in which a reaction is written influences the value of the enthalpy change for the reaction. Many reactions are reversible, meaning that the product(s) of the reaction are capable of combining and reforming the reactant(s). If a reaction is written in the reverse direction, the sign of the ΔH changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate.

$$\mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \rightarrow \mathrm{CaCO_3}\,(s) + 177.8\ \mathrm{kJ}$$

The reaction is exothermic and thus the sign of the enthalpy change is negative.

$$\mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \rightarrow \mathrm{CaCO_3}\,(s) \quad \Delta H = -177.8\ \mathrm{kJ}$$

Stoichiometric Calculations and Enthalpy Changes

Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems. Refer again to the combustion reaction of methane. Since the reaction of 1 mol of methane released 890.4 kJ, the reaction of 2 mol of methane would release $2 \times 890.4\ \mathrm{kJ} = 1781\ \mathrm{kJ}$. The reaction of 0.5 mol of methane would release $\frac{890,4\ \mathrm{kJ}}{2} = 445.2\ \mathrm{kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

Example 9.8.1

Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction, according to the following thermochemical equation.

$$2\mathrm{SO_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{SO_3}\,(g) + 198\ \mathrm{kJ}$$

Calculate the enthalpy change that occurs when $58.0\ \text{g}$ of sulfur dioxide is reacted with excess oxygen.

Solution

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

- Mass $\text{SO}_2 = 58.0\ \text{g}$
- Molar mass $\text{SO}_2 = 64.07\ \text{g/mol}$
- $\Delta H = -198\ \text{kJ}$ for the reaction of $2\ \text{mol}\ \text{SO}_2$

Unknown

- $\Delta H = ?\ \text{kJ}$

The calculation requires two steps. The mass of SO_2 is converted to moles. Then the moles of SO_2 is multiplied by the conversion factor of $\left(\dfrac{-198\ \text{kJ}}{2\ \text{mol}\ \text{SO}_2}\right)$.

Step 2: Solve.

$$\Delta H = 58.0\ \text{g}\ \text{SO}_2 \times \frac{1\ \text{mol}\ \text{SO}_2}{64.07\ \text{g}\ \text{SO}_2} \times \frac{-198\ \text{kJ}}{2\ \text{mol}\ \text{SO}_2} = 89.6\ \text{kJ}$$

Step 3: Think about your result.

The mass of sulfur dioxide is slightly less than $1\ \text{mol}$. Since $198\ \text{kJ}$ is released for every $2\ \text{mol}$ of SO_2 that reacts, the heat released when about $1\ \text{mol}$ reacts is one half of 198. The $89.6\ \text{kJ}$ is slightly less than half of 198. The sign of ΔH is negative because the reaction is exothermic.

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CHAPTER OVERVIEW

10: Energy

10.1: Energy
10.2: Energy and Chemical and Physical Change
10.3: Temperature - Random Motion of Molecules and Atoms
10.4: Temperature Changes - Heat Capacity
10.5: Energy and Heat Capacity Calculations

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10.1: 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 10.1.1).



Figure 10.1.1: 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 10.1.2). 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 10.1.2: 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 $1^{\circ}\mathrm{C}$. For example, raising the temperature of $100\ \mathrm{g}$ of water from $20^{\circ}\mathrm{C}$ to $22^{\circ}\mathrm{C}$ would require $100 \times 2 = 200\ \mathrm{cal}$.

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

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

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

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

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

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

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

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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10.2: 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.

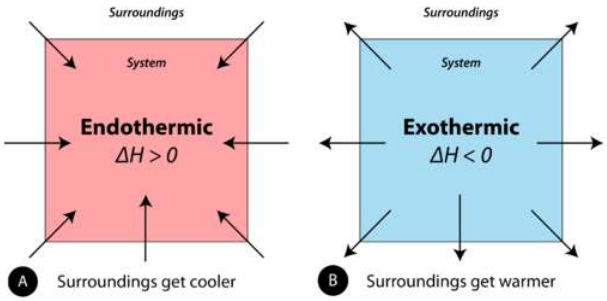


Figure 10.2.1: (A) Endothermic reaction. (B) Exothermic reaction.

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 10.2.1

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 10.2.1

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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10.3: 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 10.3.1: 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 10.3.2: 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 $32^{\circ}\mathrm{F}$ and the boiling point as $212^{\circ}\mathrm{F}$. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Scale

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

The Kelvin Scale

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

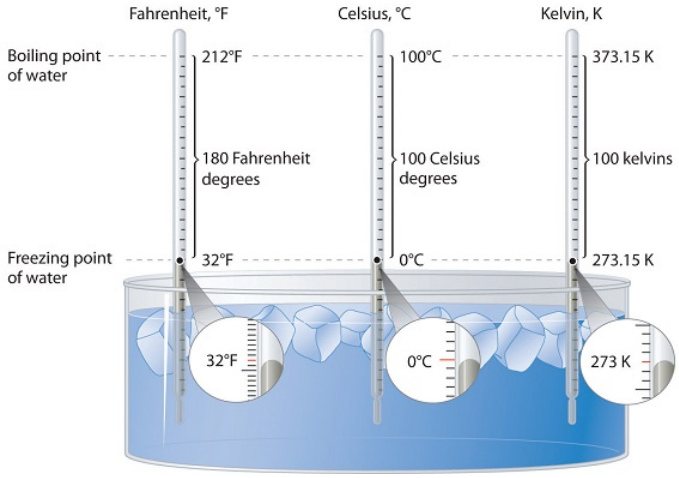


Figure 10.3.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In 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:

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

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

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:

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

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

Example 10.3.1: 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:

$$^\circ C = \frac{(103.5^\circ F - 32)}{1.8} \tag{10.3.1}$$

$$= 39.7\,^\circ C \tag{10.3.2}$$

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

$$K = 39.7\ ^{\circ}C + 273.15 \quad (10.3.3)$$
$$= 312.9\ K \quad (10.3.4)$$

? Exercise 10.3.1

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).

Contributions & Attributions

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10.4: Temperature Changes - Heat Capacity

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends on both its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the wading pool.

Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$). Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $(\mathrm{J/g^{\circ}C})$ or calories per gram per degree $(\mathrm{cal/g^{\circ}C})$ (Table $10.4.1$). This text will use $\mathrm{J/g^{\circ}C}$ for specific heat.

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

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

Table 10.4.1: Specific Heat Capacities

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

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



Figure 10.4.1: 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.

Summary

- Heat capacity is the amount of heat required to raise the temperature of an object by $1^{o}C$).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{o}C$.

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10.5: Energy and Heat Capacity Calculations

Learning Objectives

- To relate heat transfer to temperature change.

Heat is a familiar manifestation of transferring energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat (q) to specific heat (c_p), mass (m), and temperature change (ΔT) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature.

Every substance has a characteristic specific heat, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express Δ*T*. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°. Table $10.5.1$lists the specific heats for various materials.

Table 10.5.1*: Specific Heats of Some Common Substances*

Substance	**Specific Heat** $(\mathrm{J/g^oC})$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

The *direction* of heat flow is not shown in heat = *mc*Δ*T*. If energy goes into an object, the total energy of the object increases, and the values of heat Δ*T* are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and Δ*T* are negative.

Example 10.5.1

A 15.0 g piece of cadmium metal absorbs 134 J of heat while rising from 24.0°C to 62.7°C. Calculate the specific heat of cadmium.

Solution

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

Known

- Heat $= q = 134$ J
- Mass $= m = 15.0$ g
- $\Delta T = 62.7^{\circ}\text{C} - 24.0^{\circ}\text{C} = 38.7^{\circ}\text{C}$

Unknown

- c_p of cadmium $=?\ \text{J/g}^{\circ}\text{C}$

The specific heat equation can be rearranged to solve for the specific heat.

Step 2: Solve.

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7^{\circ}\text{C}} = 0.231\ \text{J/g}^{\circ}\text{C}$$

Step 3: Think about your result.

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known (Table 10.5.1), they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that a 60.0 g of water at 23.52°C was cooled by the removal of 813 J of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g}^{\circ}\text{C} \times 60.0\ \text{g}} = 3.24^{\circ}\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^{\circ}\text{C} - 3.24^{\circ}\text{C} = 20.28^{\circ}\text{C}$$

Example 10.5.2

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

Solution

We can use heat = $mc\Delta T$ to determine the amount of heat, but first we need to determine ΔT. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 73.3^{\circ}\text{C} - 25.0^{\circ}\text{C} = 48.3^{\circ}\text{C}$$

The mass is given as 150.0 g, and Table 7.3 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into heat = $mc\Delta T$ and solve for amount of heat:

$$\text{heat} = (150.0\ \text{g})\left(0.108\ \frac{\text{cal}}{\text{g} \cdot {}^{\circ}\text{C}}\right)(48.3^{\circ}\text{C}) = 782\ \text{cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

Exercise 10.5.1

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

Answer

Heat leaves the aluminum block.

Example 10.5.2

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 10.5.1?

Solution

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0°\text{C} - 97.5°\text{C} = -75.5°\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, −71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for c:

$$-71.7 \text{ cal} = (10.3 \text{ g})(c)(-75.5°\text{C})$$

$$c = \frac{-71.7 \text{ cal}}{(10.3 \text{ g})(-75.5°\text{C})}$$

$$c = 0.0923 \text{ cal/g•°C}$$

This value for specific heat is very close to that given for copper in Table 7.3.

Exercise 10.5.2

A 10.7 g crystal of sodium chloride (NaCl) has an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

Answer

Summary

Specific heat calculations are illustrated.

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CHAPTER OVERVIEW

11: Modern Atomic Theory

11.1: Light- Electromagnetic Radiation
11.2: The Electromagnetic Spectrum
11.3: The Bohr Model - Atoms with Orbits
11.4: The Quantum-Mechanical Model- Atoms with Orbitals
11.5: Quantum-Mechanical Orbitals and Electron Configurations
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11.7: The Explanatory Power of the Quantum-Mechanical Model
11.8: Periodic Trends - Atomic Size, Ionization Energy, and Metallic Character
11.E: Electrons in Atoms and the Periodic Table (Exercises)

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11.1: Light- Electromagnetic Radiation

Learning Objectives

- Define the terms wavelength and frequency with respect to wave-form energy.
- State the relationship between wavelength and frequency with respect to electromagnetic radiation.

During the summer, almost everyone enjoys going to the beach. Beach-goers can swim, have picnics, and work on their tans. But if a person gets too much sun, they can burn. A particular set of solar wavelengths are especially harmful to the skin. This portion of the solar spectrum is known as UV B, with wavelengths of 280-320 nm. Sunscreens are effective in protecting skin against both the immediate skin damage and the long-term possibility of skin cancer.

Waves

Waves are characterized by their repetitive motion. Imagine a toy boat riding the waves in a wave pool. As the water wave passes under the boat, it moves up and down in a regular and repeated fashion. While the wave travels horizontally, the boat only travels vertically up and down. The figure below shows two examples of waves.

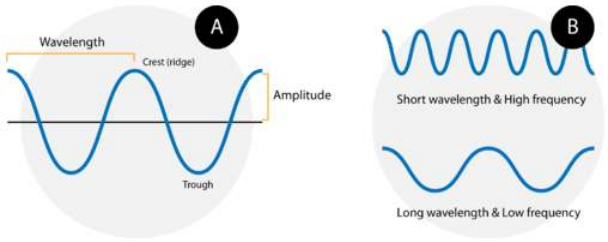


Figure 11.1.1: (A) A wave consists of alternation crests and troughs. The wavelength (λ) is defined as the distance between any two consecutive identical points on the waveform. The amplitude is the height of the wave. (B) A wave with a short wavelength (top) has a high frequency because more waves pass a given point in a certain amount of time. A wave with a longer wavelength (bottom) has a lower frequency.

A wave cycle consists of one complete wave—starting at the zero point, going up to a wave **crest**, going back down to a wave **trough**, and back to the zero point again. The **wavelength** of a wave is the distance between any two corresponding points on adjacent waves. It is easiest to visualize the wavelength of a wave as the distance from one wave crest to the next. In an equation, wavelength is represented by the Greek letter lambda (λ). Depending on the type of wave, wavelength can be measured in meters, centimeters, or nanometers $\left(1\ \text{m} = 10^9\ \text{nm}\right)$. The **frequency**, represented by the Greek letter nu (ν), is the number of waves that pass a certain point in a specified amount of time. Typically, frequency is measured in units of cycles per second or waves per second. One wave per second is also called a Hertz (Hz) and in SI units is a reciprocal second $\left(\text{s}^{-1}\right)$.

Figure B above shows an important relationship between the wavelength and frequency of a wave. The top wave clearly has a shorter wavelength than the second wave. However, if you picture yourself at a stationary point watching these waves pass by, more waves of the first kind would pass by in a given amount of time. Thus the frequency of the first wave is greater than that of the second wave. Wavelength and frequency are therefore inversely related. As the wavelength of a wave increases, its frequency decreases. The equation that relates the two is:

$$c = \lambda\nu$$

The variable c is the speed of light. For the relationship to hold mathematically, if the speed of light is used in m/s, the wavelength must be in meters and the frequency in Hertz.

Example 11.1.1: Orange Light

The color orange within the visible light spectrum has a wavelength of about 620 nm. What is the frequency of orange light?

Solution

Solutions to Example 9.2.1

Steps for Problem Solving	Example 11.1.1

Steps for Problem Solving	Example 11.1.1
Identify the "given" information and what the problem is asking you to "find."	Given : • Wavelength $(\lambda) = 620\ \text{nm}$ • Speed of light $(c) = 3.00 \times 10^8\ \text{m/s}$ Find: Frequency (Hz)
List other known quantities.	$1\ \text{m} = 10^9\ \text{nm}$
Identify steps to get the final answer.	1.Convert the wavelength to m. 2. Apply the equation $c = \lambda\nu$ and solve for frequency. Dividing both sides of the equation by λ yields: $\nu = \frac{c}{\lambda}$
Cancel units and calculate.	$620\ \text{nm} \times \left(\frac{1\ \text{m}}{10^9\ \text{nm}}\right) = 6.20 \times 10^{-7}\ \text{m}$ $\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8\ \text{m/s}}{6.20 \times 10^{-7}} = 4.8 \times 10^{14}\ \text{Hz}$
Think about your result.	The value for the frequency falls within the range for visible light.

? Exercise 11.1.1

What is the wavelength of light if its frequency is $1.55 \times 10^{10}\ \text{s}^{-1}$?

Answer

0.0194 m, or 19.4 mm

Summary

All waves can be defined in terms of their frequency and intensity. $c = \lambda\nu$ expresses the relationship between wavelength and frequency.

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11.2: 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 11.2.1 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.

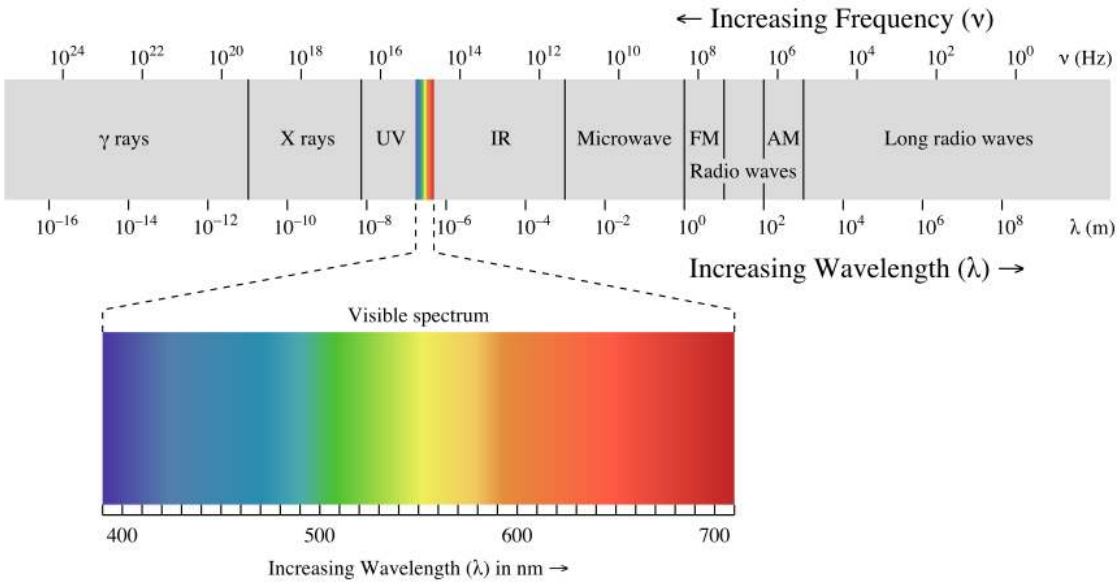


Figure 11.2.1: The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate. (CC BY-NC-SA; anonymous by request).

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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11.3: 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 11.3.1: 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 11.3.2: 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.

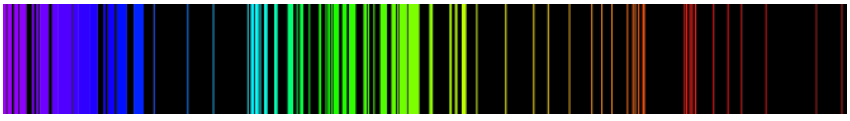


Figure 11.3.3: Atomic Emission Spectrum of Iron.

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 11.3.3: 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.

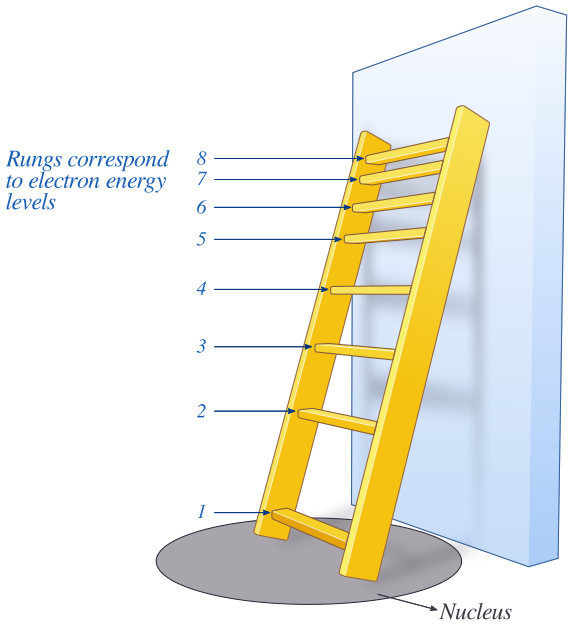


Figure 11.3.4: The energy levels of the electrons can be viewed as rungs on a ladder. Note that the spacing between rungs gets smaller at higher energies (CC BY-NC; Ümit Kaya)

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.

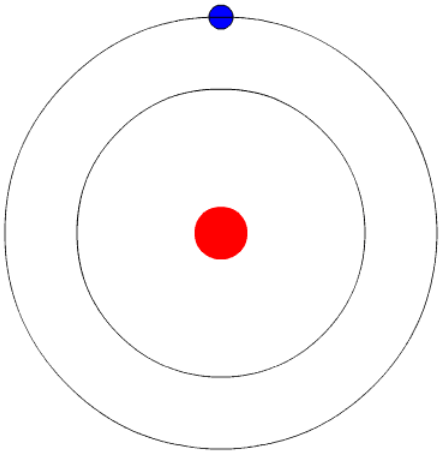


Figure 11.3.5: In Bohr's Model of the atom, electrons absorb energy to move to a higher level and release energy to move to lower levels. (CC BY-SA 3.0; Kurzon).

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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11.4: 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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11.5: 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:

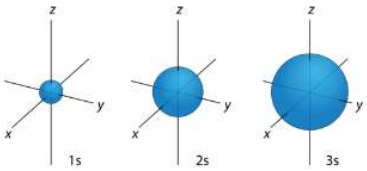


Figure 11.5.1: s orbitals have no orientational preference and resemble spheres.

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.

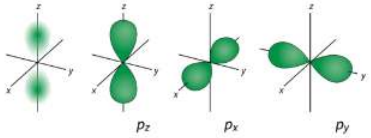


Figure 11.5.2: p orbitals have an orientational preference and resemble dumbbells.

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.

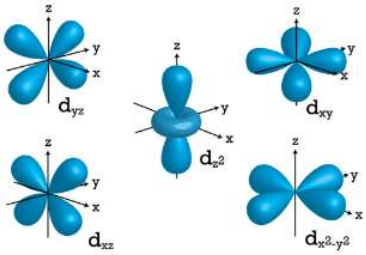


Figure 11.5.3: d orbitals have an orientational preference and exhibit complex structures.

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.

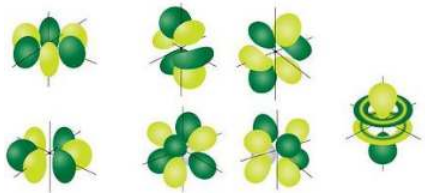


Figure 11.5.4: f orbitals have an orientational preference and exhibit quite complex structures.

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 11.5.1.

Table 11.5.1: 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

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

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

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

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

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

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 $11.5.1$ shows the electron configurations of the elements in the second period.

Table 11.5.2: 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 $11.5.5$ 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.

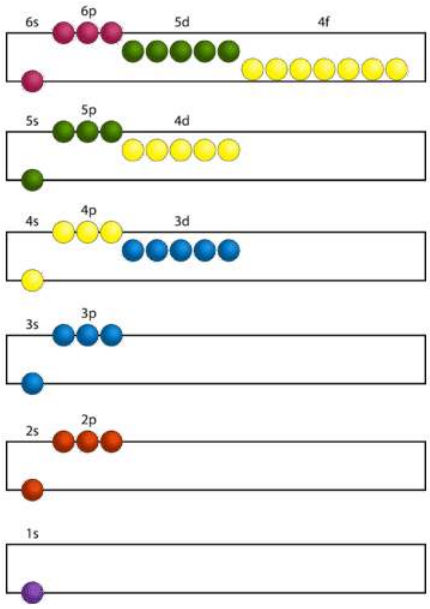


Figure 11.5.5: Electrons are added to atomic orbitals in order from low energy (bottom of the graph) to high (top of the graph) according to the Aufbau principle. Principle energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding two electrons.

As seen in the figure above, the energies of the sublevels in different principal energy levels eventually begin to overlap. After the $3p$ sublevel, it would seem logical that the $3d$ sublevel should be the next lowest in energy. However, the $4s$ sublevel is slightly lower in energy than the $3d$ sublevel and thus fills first. Following the filling of the $3d$ sublevel is the $4p$, then the $5s$ and the $4d$. Note that the $4f$ sublevel does not fill until just after the $6s$ sublevel. Figure $11.5.6$ is a useful and simple aid for keeping track of the order of fill of the atomic sublevels.

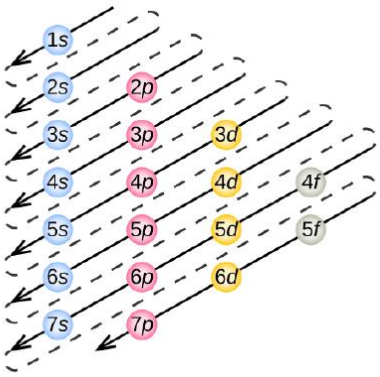


Figure 11.5.6: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.



Video 11.5.1: Energy levels, sublevels and orbitals.

Example 11.5.1: Nitrogen Atoms

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

Solution:

Take a close look at Figure 11.5.5, 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 11.5.2: Potassium Atoms

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

Solution

This time, take a close look at Figure 11.5.5

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 11.5.1: 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 $1s$ 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 $11.5.7$ shows how the electrons are indicated in a diagram.

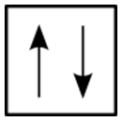


Figure 11.5.7: In an orbital filling diagram, a square represents an orbital, while arrows represent electrons. An arrow pointing upward represents one spin direction, while an arrow pointing downward represents the other spin direction.

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.

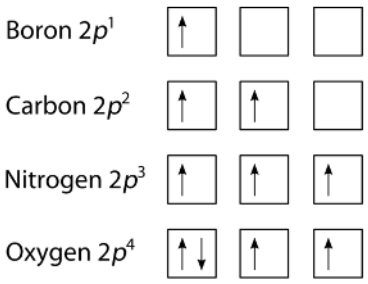


Figure 11.5.8: The $2p$ sublevel, for the elements boron $(Z = 5)$, carbon $(Z = 6)$, nitrogen $(Z = 7)$, and oxygen $(Z = 8)$. According to Hund's rule, as electrons are added to a set of orbitals of equal energy, one electron enters each orbital before any orbital receives a second electron.

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.

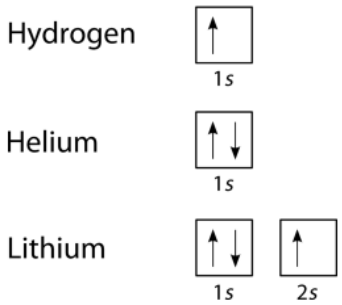


Figure 11.5.9: Orbital filling diagrams for hydrogen, helium, and lithium.

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 $11.5.10$ There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital.

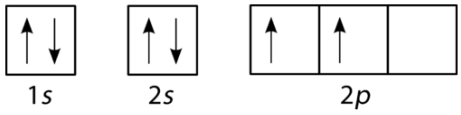


Figure 11.5.10: Orbital filling diagram for carbon.

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.

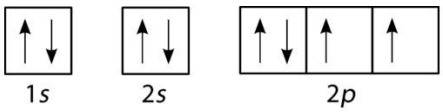


Figure 11.5.11: Orbital filling diagram for oxygen.

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 11.5.3: Carbon Atoms

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

Solution

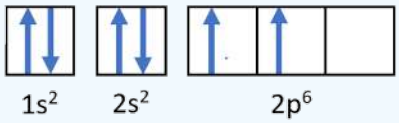
Step 1: List the known quantities and plan the problem.

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.

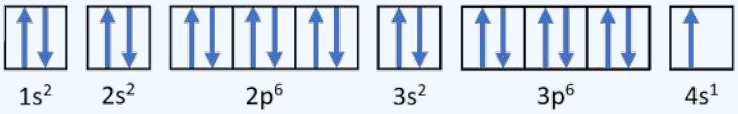
Exercise 11.5.2: Electronic Configurations

Write the electron configurations and orbital diagrams for

a. Potassium atom: K
b. Arsenic atom: As
c. Phosphorus atom: P

Answer a:

Potassium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$



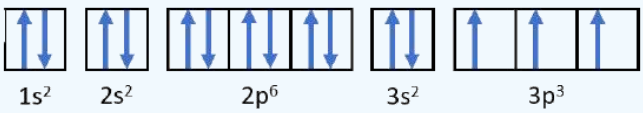
Answer b:

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

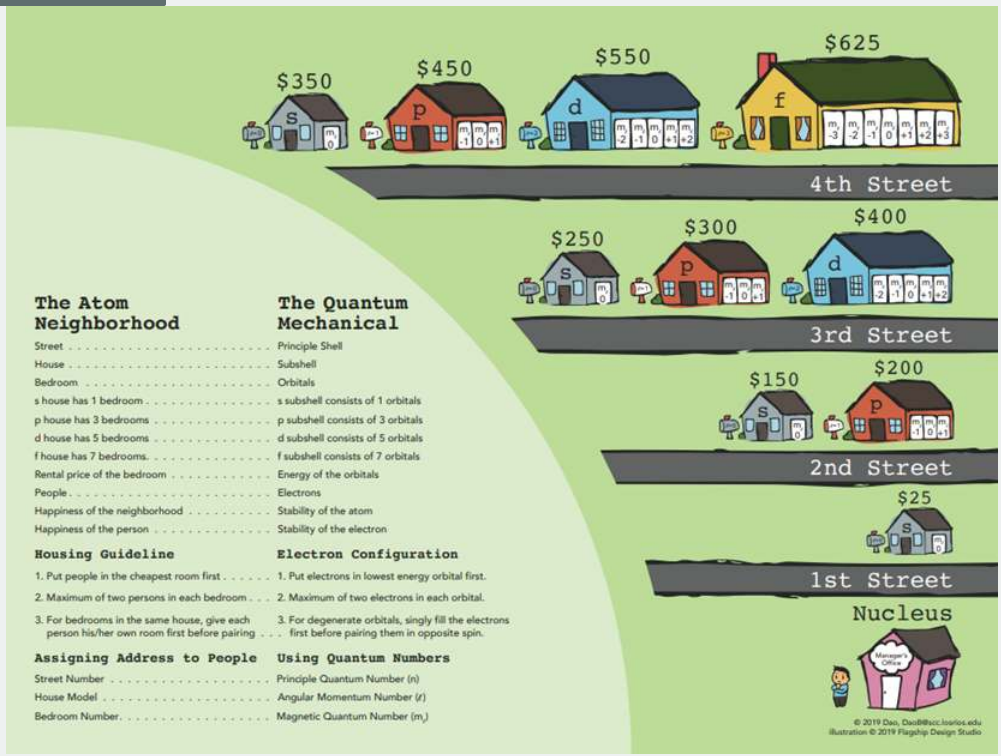


Figure 11.5.12: The atom neighborhood. Source: Dr. Binh Dao, Sacramento City College.

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

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

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11.6: 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 11.6.1. 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.

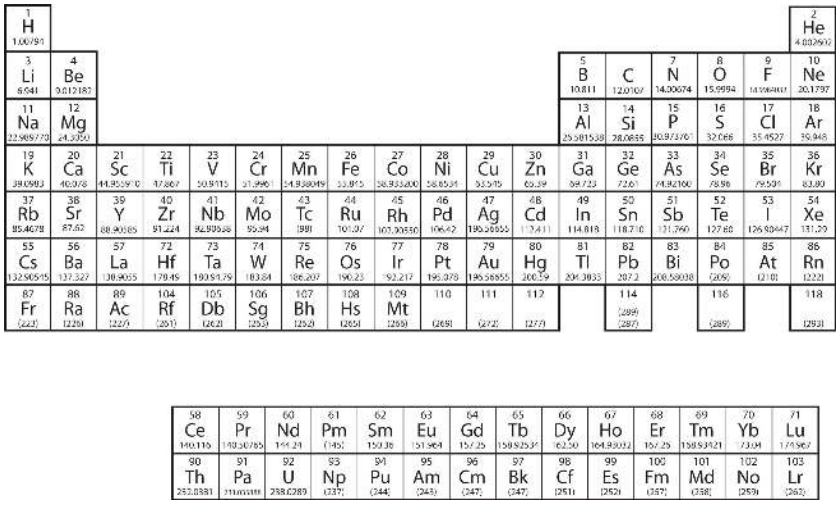


Figure 11.6.1: The Periodic Table

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 11.6.2)

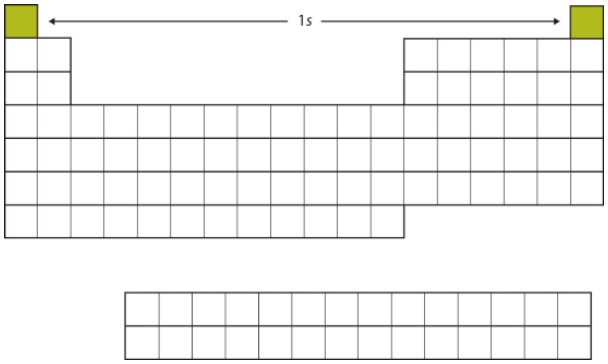


Figure 11.6.2: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 11.6.3 shows that these two elements are adjacent on the periodic table.

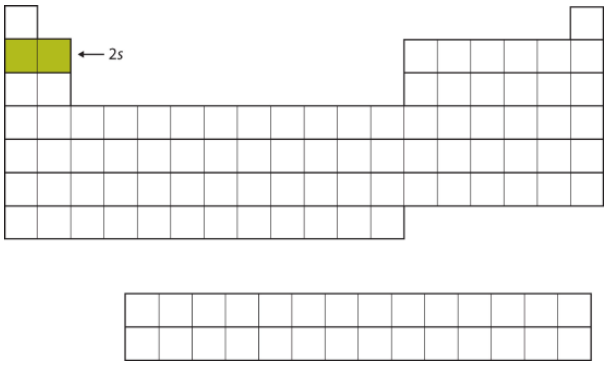


Figure 11.6.3: The 2*s* Subshell. In Li and Be, the 2*s* subshell is being filled.

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 11.6.4).

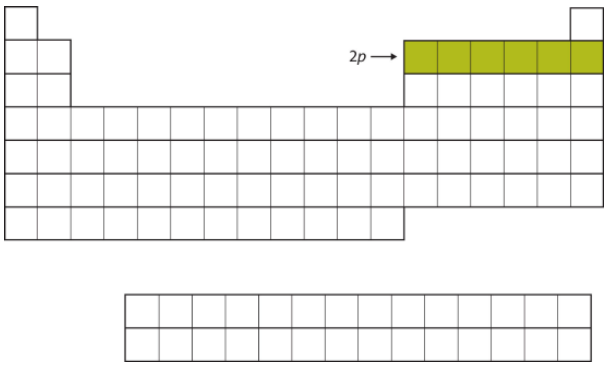


Figure 11.6.4: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

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 11.6.5).

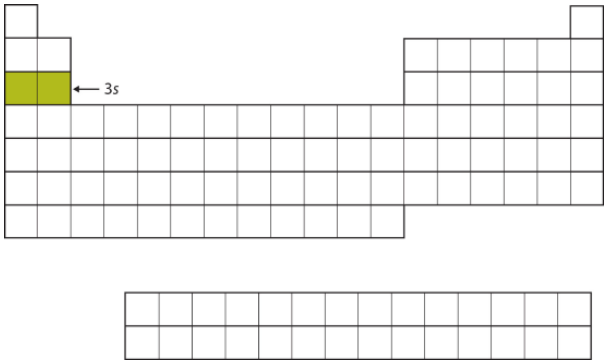


Figure 11.6.5: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 11.6.6).

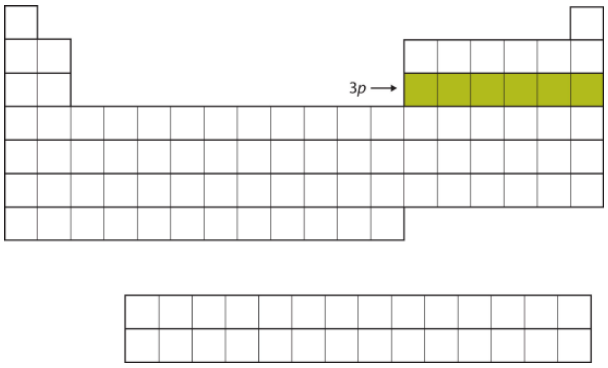


Figure 11.6.6: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 11.6.7).

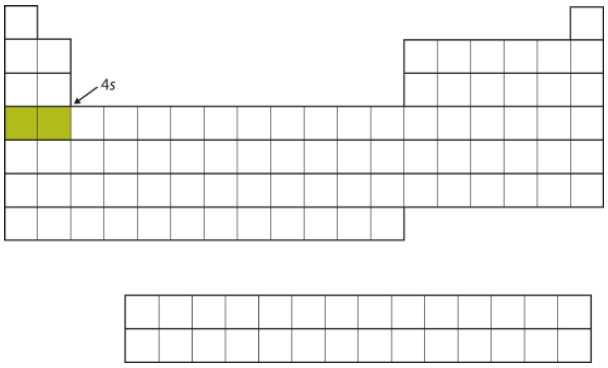


Figure 11.6.7: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

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 11.6.8).

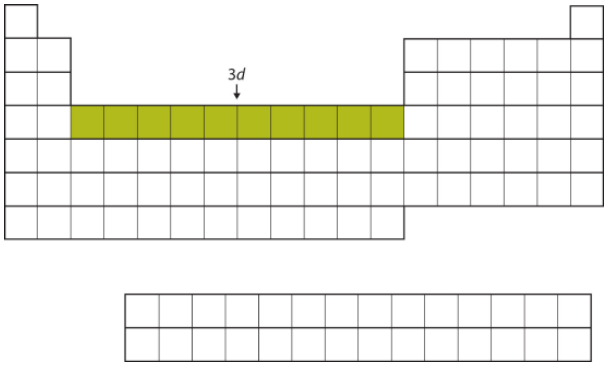


Figure 11.6.8: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

...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 11.6.9 shows the blocks of the periodic table.

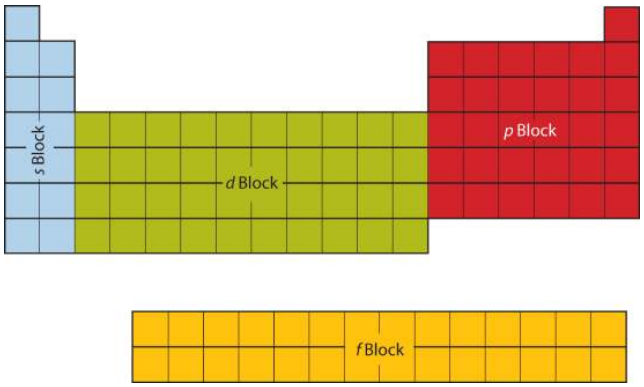


Figure 11.6.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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

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

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

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 11.6.10 It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

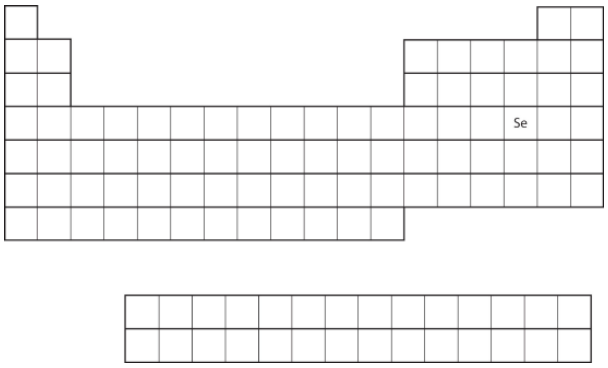


Figure 11.6.10: Selenium on the Periodic Table

Example 11.6.1: Predicting Electron Configurations

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 11.6.11).

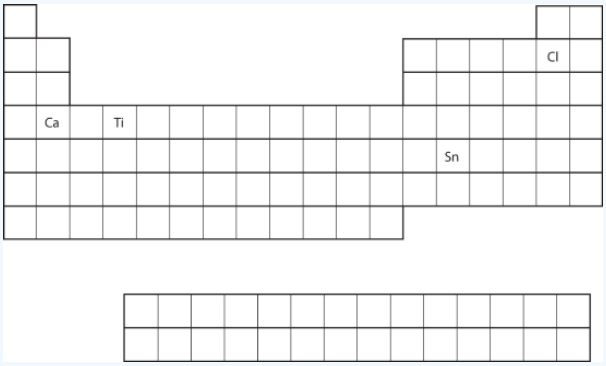


Figure 11.6.11: Various Elements on the Periodic Table

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 11.6.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 11.6.11.

a. Ti
b. Cl

Answer a

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

Answer b

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

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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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11.7: The Explanatory Power of the Quantum-Mechanical Model

Learning Objectives

- Give the name and location of specific groups on the periodic table, including alkali metals, alkaline earth metals, noble gases, halogens, and transition metals.
- Explain the relationship between the chemical behavior of families in the periodic table and their electron configurations.
- Identify elements that will have the most similar properties to a given element.

The chemical behavior of atoms is controlled by their electron configuration. Since the families of elements were organized by their chemical behavior, it is predictable that the individual members of each chemical family will have similar electron configurations.

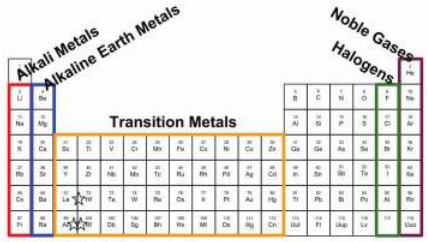
Families of the Periodic Table

Remember that Mendeleev arranged the periodic table so that elements with the most similar properties were placed in the same group. A **group** is a vertical column of the periodic table. All of the 1A elements have one valence electron. This is what causes these elements to react in the same ways as the other members of the family. The elements in 1A are all very reactive and form compounds in the same ratios with similar properties with other elements. Because of their similarities in their chemical properties, Mendeleev put these elements into the same group. Group 1A is also known as the **alkali metals**. Although most metals tend to be very hard, these metals are actually soft and can be easily cut.

Group 2A is also called the **alkaline earth metals**. Once again, because of their similarities in electron configurations, these elements have similar properties to each other. The same pattern is true of other groups on the periodic table. Remember, Mendeleev arranged the table so that elements with the most similar properties were in the same group on the periodic table.

It is important to recognize a couple of other important groups on the periodic table by their group name. Group 7A (or 17) elements are also called **halogens**. This group contains very reactive nonmetal elements.

The **noble gases** are in group 8A. These elements also have similar properties to each other, the most significant property being that they are extremely unreactive, rarely forming compounds. The reason for this will be communicated later, when we discuss how compounds form. The elements in this group are also gases at room temperature.

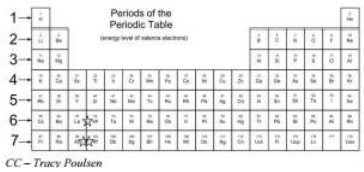


Families of the periodic table.
CC – Tracy Poulsen

An alternate numbering system numbers all of the s, p, and d block elements from 1-18. In this numbering system, group 1A is group 1; group 2A is group 2; the halogens (7A) are group 17; and the noble gases (8A) are group 18. You will come across periodic tables with both numbering systems. It is important to recognize which numbering system is being used, and to be able to find the number of valence electrons in the main block elements, regardless of which numbering system is being used.

Periods of the Periodic Table

If you can locate an element on the Periodic Table, you can use the element's position to figure out the energy level of the element's valence electrons. A **period** is a horizontal row of elements on the periodic table. For example, the elements sodium (Na) and magnesium (Mg) are both in period 3. The elements astatine (At) and radon (Rn) are both in period 6.



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Summary

- The vertical columns on the periodic table are called groups or families because of their similar chemical behavior.
- All the members of a family of elements have the same number of valence electrons and similar chemical properties.
- The horizontal rows on the periodic table are called periods.

Vocabulary

- **Group (family)** - A vertical column of the periodic table.
- **Alkali metals** - Group 1A of the periodic table.
- **Alkaline earth metals** - Group 2A of the periodic table.
- **Halogens** - Group 7A of the periodic table.
- **Noble gases** - Group 8A of the periodic table.
- **Transition elements** - Groups 3 to 12 of the periodic table.

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11.8: Periodic Trends - Atomic Size, Ionization Energy, and Metallic Character

Learning Objectives

- Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variations of properties versus positions on the periodic table are called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row or down a whole column of the periodic table.

The first periodic trend we will consider is atomic radius. The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. This trend can be summarized as follows:

$$as \downarrow PT, atomic\ radius \uparrow$$

where PT stands for periodic table. Going across a row on the periodic table, left to right, the trend is different. Even though the valence shell maintains the same principal quantum number, the number of protons—and hence the nuclear charge—is increasing as you go across the row. The increasing positive charge casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease. Again, we can summarize this trend as follows:

$$as \rightarrow PT, atomic\ radius \downarrow$$

Figure 11.8.1 shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

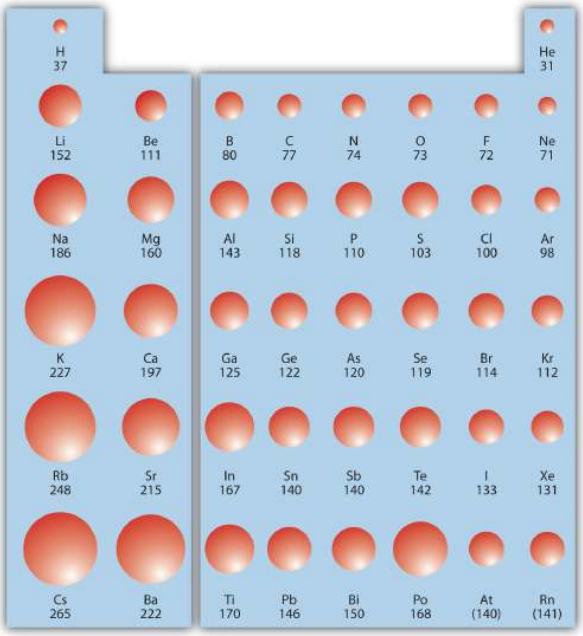


Figure 11.8.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

Example 11.8.1: Atomic Radii

Referring only to a periodic table and not to Figure 11.8.1, which atom is larger in each pair?

a. Si or S
b. S or Te

Solution

a. Si is to the left of S on the periodic table; it is larger because as you go across the row, the atoms get smaller.
b. S is above Te on the periodic table; Te is larger because as you go down the column, the atoms get larger.

Exercise 11.8.1: Atomic Radii

Referring only to a periodic table and not to Figure 11.8.1, which atom is smaller, Ca or Br?

Answer

Br

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \Delta H \equiv IE$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

$$as \downarrow PT,\ IE \downarrow$$

However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron; as a result, IE increases:

$$as \rightarrow PT,\ IE \uparrow$$

Figure 11.8.2shows values of IE versus position on the periodic table. Again, the trend is not absolute, but the general trends going across and down the periodic table should be obvious.

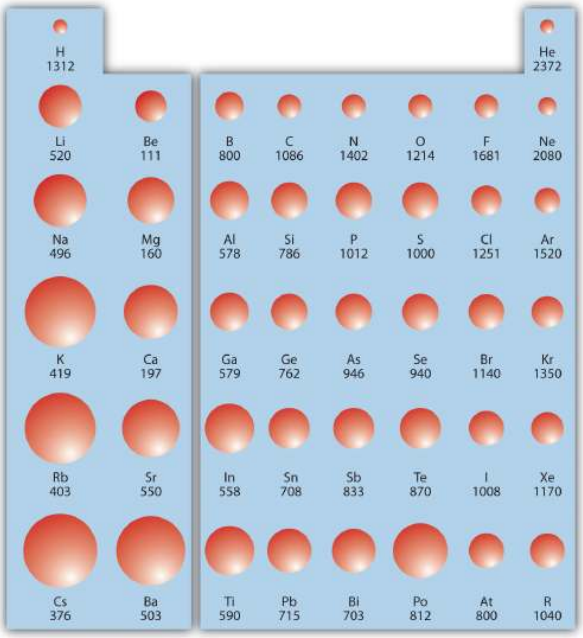


Figure 11.8.2: Ionization Energy on the Periodic Table. Values are in kJ/mol.

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

- First Ionization Energy (IE_1):

$$A(g) \rightarrow A^+(g) + e^-$$

- Second Ionization Energy (IE_2):

$$A^+(g) \rightarrow A^{2+}(g) + e^-$$

- Third Ionization Energy (IE_3):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^-$$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^2 2s^2 2p^6 3s^2$:

- First Ionization Energy (IE_1) = 738 kJ/mol:

$$\mathrm{Mg(g) \longrightarrow Mg^+(g) + e-}$$

- Second Ionization Energy (IE_2) = 1,450 kJ/mol:

$$\mathrm{Mg^+(g) \longrightarrow Mg^{2+}(g) + e-}$$

- Third Ionization Energy (IE_3) = 7,734 kJ/mol:

$$\mathrm{Mg^{2+}(g) \longrightarrow Mg^{3+}(g) + e-}$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the $n = 2$ shell (specifically, the 2*p* subshell, which is lower in energy than the $n = 3$ shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. It is trends like this that demonstrate that electrons within atoms are organized in groups.

✔ Example 11.8.2: Ionization Energies

Which atom in each pair has the larger first ionization energy?

a. Ca or Sr
b. K or K^+

Solution

a. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
b. Because K^+ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K^+ to be removed comes from another shell.

? Exercise 11.8.2: Ionization Energies

Which atom has the lower ionization energy, C or F?

Answer

C

The opposite of IE is described by **electron affinity (EA),** which is the energy change when a gas-phase atom accepts an electron:

$$\mathrm{A(g) + e^- \longrightarrow A^-(g)} \qquad \Delta H \equiv EA$$

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$as \rightarrow PT,\ EA \uparrow$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure 11.8.3 shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend is not absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

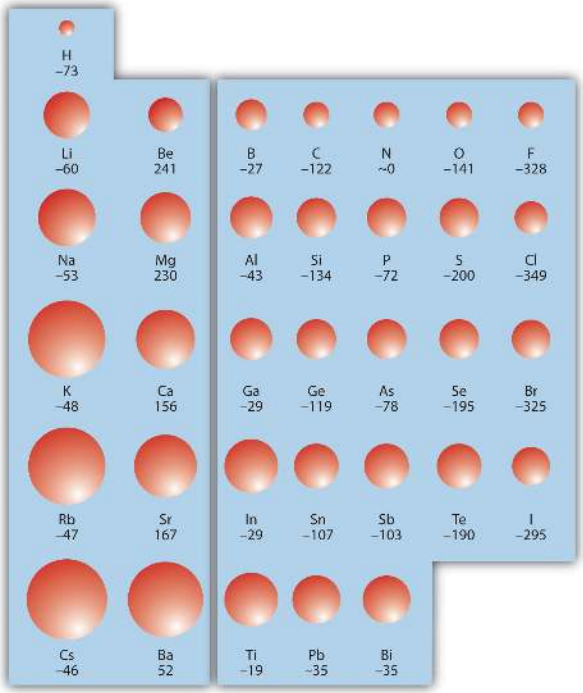


Figure 11.8.3: Electron Affinity on the Periodic Table. Values are in kJ/mol.

Example 11.8.3: Electron Affinities

Predict which atom in each pair will have the highest magnitude of Electron Affinity.

a. C or F
b. Na or S

Solution

a. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
b. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

Exercise 11.8.3: Electron Affinities

Predict which atom will have the highest magnitude of Electron Affinity: As or Br.

Answer

Br

Metallic Character

The metallic character is used to define the chemical properties that metallic elements present. Generally, metals tend to lose electrons to form cations. Nonmetals tend to gain electrons to form anions. They also have a high oxidation potential—therefore they are easily oxidized and are strong reducing agents. Metals also form basic oxides; the more basic the oxide, the higher the metallic character.

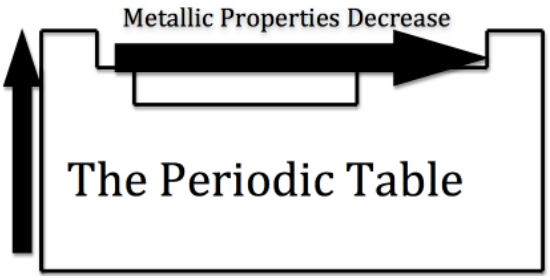


Figure 11.8.4: Courtesy of Jessica Thornton (UCD)

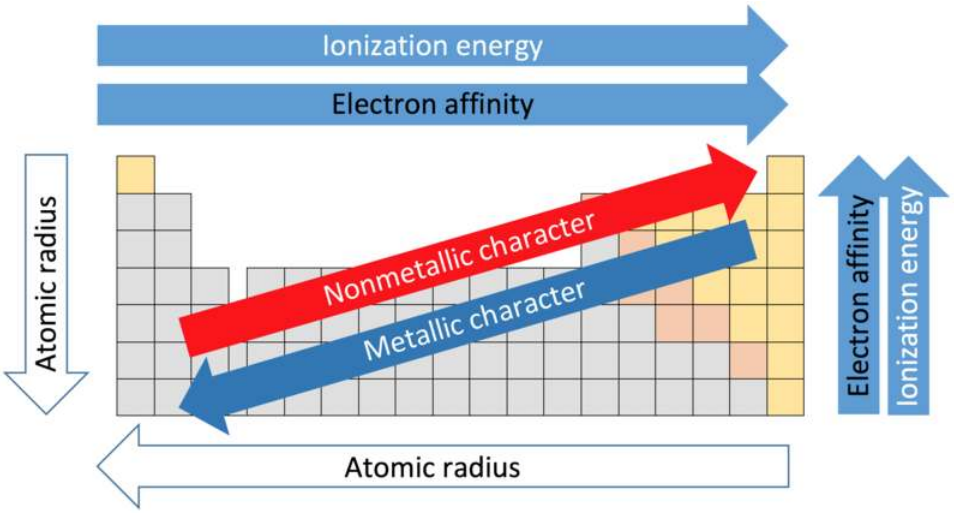
As you move across the table from left to right, the metallic character decreases, because the elements easily accept electrons to fill their valance shells. Therefore, these elements take on the nonmetallic character of forming anions. As you move up the table, the metallic character decreases, due to the greater pull that the nucleus has on the outer electrons. This greater pull makes it harder for the atoms to lose electrons and form cations.

Uses of the Periodic Properties of Elements

1. Predict greater or smaller atomic size and radial distribution in neutral atoms and ions.
2. Measure and compare ionization energies.
3. Compare electron affinities and electronegativities.
    - Predict redox potential.
    - Compare metallic character with other elements; ability to form cations.
    - Predict reactions that may or may not occur due to the trends.
    - Determine greater cell potential (sum of oxidation and reduction potential) between reactions.
    - Complete chemical reactions according to trends.

Summary

- Certain properties—notably atomic radius, ionization energies, and electron affinities—can be qualitatively understood by the positions of the elements on the periodic table. The major trends are summarized in the figure below.
- There are three factors that help in the prediction of the trends in the Periodic Table: number of protons in the nucleus, number of shells, and shielding effect.



Various periodic trends (CC BY-SA 4.0; Sandbh via Wikipedia)

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11.E: Electrons in Atoms and the Periodic Table (Exercises)

9.1: Blimps, Balloons, and Models of the Atom

9.2: Light: Electromagnetic Radiation

9.3: The Electromagnetic Spectrum

1. Choose the correct word for the following statement. Blue light has a (longer or shorter) wavelength than red light.
2. Choose the correct word for the following statement. Yellow light has a (higher or lower) frequency than blue light.
3. Choose the correct word for the following statement. Green light has a (larger or smaller) energy than red light.
4. If "light A" has a longer wavelength than "light B", then "light A" has _____ "light B".

    (a) a lower frequency than

    (b) a higher frequency than

    (c) the same frequency as

5. If "light C" has a shorter wavelength than "light D", then "light C" has _____ "light D".

    (a) a larger energy than

    (b) a smaller energy than

    (c) the same energy as

6. If "light E" has a higher frequency than "light F", then "light E" has _____ "light F".

    (a) a longer wavelength than

    (b) a shorter wavelength than

    (c) the same wavelength as

7. If "light G" has a higher frequency than "light H", then "light G" has _____ "light H".

    (a) a larger energy than

    (b) a smaller energy than

    (c) the same energy as

8. If "light J" has larger energy than "light K", then "light J" has _____ "light K".

    (a) a shorter wavelength than

    (b) a longer wavelength than

    (c) the same wavelength as

9. Which of the following statements is true?

    (a) The frequency of green light is higher than the frequency of blue light and the wavelength of green light is longer than the wavelength of blue light.

    (b) The frequency of green light is higher than the frequency of blue light and the wavelength of green light is shorter than the wavelength of blue light.

    (c) The frequency of green light is lower than the frequency of blue light and the wavelength of green light is shorter than the wavelength of blue light.

    (d) The frequency of green light is lower than the frequency of blue light and the wavelength of green light is longer than the wavelength of blue light.

    (e) The frequency of green light is the same as the frequency of blue light and the wavelength of green light is shorter than the wavelength of blue light.

10. As the wavelength of electromagnetic radiation increases:

    (a) its energy increases.

    (b) its frequency increases.

    (c) its speed increases.

    (d) more than one of the above statements is true.

    (e) none of the above statements is true.

11. List three examples of electromagnetic waves.
12. Why do white objects appear white?
13. Name the colors present in white light in order of increasing frequency.
14. Why do objects appear black?

9.4: The Bohr Model: Atoms with Orbits

1. Decide whether each of the following statements is true or false:

    (a) Niels Bohr suggested that the electrons in an atom were restricted to specific orbits and thus could only have certain energies.

    (b) Bohr's model of the atom can be used to accurately predict the emission spectrum of hydrogen.

    (c) Bohr's model of the atom can be used to accurately predict the emission spectrum of neon.

    (d) According to the Bohr model, electrons have more or less energy depending on how far around an orbit they have traveled.

2. According to the Bohr model, electrons in an atom can only have certain, allowable energies. As a result, we say that the energies of these electrons are _____.
3. The Bohr model accurately predicts the emission spectra of atoms with…

    (a) less than 1 electron.

    (b) less than 2 electrons.

    (c) less than 3 electrons.

    (d) less than 4 electrons.

4. Consider an He^+ atom. Like the hydrogen atom, the He+ atom only contains 1 electron, and thus can be described by the Bohr model. Fill in the blanks in the following statements.

    (a) An electron falling from the $n = 2$ orbit of He^+ to the $n = 1$ orbit of He^+ releases _____ energy than an electron falling from the $n = 3$ orbit of He^+ to the $n = 1$ orbit of He^+.

    (b) An electron falling from the $n = 2$ orbit of He^+ to the $n = 1$ orbit of He^+ produces light with a _____ wavelength than the light produced by an electron falling from the $n = 3$ orbit of He^+ to the $n = 1$ orbit of He^+.

    (c) An electron falling from the $n = 2$ orbit of He^+ to the $n = 1$ orbit of He^+ produces light with a _____ frequency than the light produced by an electron falling from the $n = 3$ orbit of He^+ to the $n = 1$ orbit of He^+.

5. According to the Bohr model, higher energy orbits are located (closer to/further from) the atomic nucleus. This makes sense since negative electrons are (attracted to/repelled from) the positive protons in the nucleus, meaning it must take energy to move the electrons (away from/towards) the nucleus of the atom.
6. According to the Bohr model, what is the energy of an electron in the first Bohr orbit of hydrogen?
7. According to the Bohr model, what is the energy of an electron in the tenth Bohr orbit of hydrogen?
8. According to the Bohr model, what is the energy of an electron in the seventh Bohr orbit of hydrogen?
9. If an electron in a hydrogen atom has an energy of -6.06×10^{-20} J, which Bohr orbit is it in?
10. If an electron in a hydrogen atom has an energy of -2.69×10^{-20} J, which Bohr orbit is it in?
11. If an electron falls from the 5th Bohr orbital of hydrogen to the 3rd Bohr orbital of hydrogen, how much energy is released (you can give the energy as a positive number)?

12. If an electron falls from the 6th Bohr orbital of hydrogen to the 3rd Bohr orbital of hydrogen, what wavelength of light is emitted? Is this in the visible light range?

9.5: The Quantum-Mechanical Model: Atoms with Orbitals

9.6: Quantum-Mechanical Orbitals and Electron Configurations

1. Match each quantum number with the property that they describe.

Match each quantum number with the property that they describe.

(a) n	i. shape
(b) ℓ	ii. orientation in space
(c) m_l	iii. number of nodes

2. A point in an electron wave where there is zero electron density is called a _____.
3. Choose the correct word in each of the following statements.

   (a) The (higher/lower) the value of n, the more nodes there are in the electron standing wave.

   (b) The (higher/lower) the value of n, the less energy the electron has.

   (c) The (more/less) energy the electron has, the more nodes there are in its electron standing wave.

4. Fill in the blank. For lower values of n, the electron density is typically found _____ the nucleus of the atom, while for higher values of n, the electron density is typically found _____the nucleus of the atom.
5. Circle all of the statements that make sense: Schrödinger discovered that certain quantities in the electron wave equation had to be integers, because when they weren't, the wave equation described waves which…

   (a) were discontinuous

   (b) were too small

   (c) were too long and narrow

   (d) were too short and fat

   (e) "doubled back" on themselves

6. What are the allowed values of ℓ for an electron standing wave with $n = 4$?
7. How many values of ℓ are possible for an electron standing wave with $n = 9$?
8. What are the allowed values of ml for an electron standing wave with $\ell = 3$?
9. How many different orientations are possible for an electron standing wave with $\ell = 4$?
10. What are the allowed values of m_l for $n = 2$?
11. Fill in the blanks. When $\ell = 0$, the electron orbital is _____ and when $\ell = 1$, the electron orbital is _____ shaped.
12. The $n = 1$ s orbital has _____ nodes.
13. The $n = 2$ s orbital has _____ nodes.
14. The $n = 2$ p orbital has _____ nodes.
15. The $n = 1$ p orbital has _____ nodes.
16. There are ____ different p orbitals.
17. What energy level (or value of n) has s, p and d orbitals, but no f orbitals?
18. How many different d orbital orientations are there?
19. How many f orbital orientations are there?
20. How many different orbitals are there in the $n = 3$ energy level?

1. Write the electron configuration for beryllium. Beryllium has 4 electrons.
2. Write the electron configuration for silicon. Silicon has 14 electrons.
3. Write the electron configuration for nitrogen. Nitrogen has 7 electrons.
4. Write the electron configuration for chromium. Chromium has 24 electrons.
5. Write the electron configuration for silver. Silver has 47 electrons.

9.7: Electron Configurations and the Periodic Table

1. Use the Periodic Table to determine the energy level of the valence electrons in each of the following elements.

    (a) B
    (b) Ga
    (c) Rb
    (d) At
    (e) He

2. Fill in the blanks:

    (a) B is in the __ level block of the Periodic Table
    (b) Sr is in the __ level block of the Periodic Table
    (c) Fe is in the __ level block of the Periodic Table
    (d) Cs is in the __ level block of the Periodic Table
    (e) O is in the __ level block of the Periodic Table

3. Use the Periodic Table to determine the energy level and sublevel of the highest energy electrons in each of the following elements:

    (a) N
    (b) Ca
    (c) Rb
    (d) P
    (e) In

4. Decide whether each of the following statements is true or false.

    (a) Li has valence electrons in the $n = 1$ energy level.
    (b) Si has valence electrons in the $n = 3$ energy level.
    (c) Ga has valence electrons in the $n = 3$ energy level.
    (d) Xe has valence electrons in the $n = 5$ energy level.
    (e) P has valence electrons in the $n = 2$ energy level.

5. Match the element to the sublevel block it is found in:

Match the element to the sublevel block it is found in:

(a) C	i. *s* sublevel block
(b) Cs	ii. *p* sublevel block
(c) Ce	iii. *d* sublevel block
(d) Cr	iv. *f* sublevel block

6. The first row of the Periodic Table has:

    (a) 1 element
    (b) 2 elements
    (c) 3 elements
    (d) 4 elements
    (e) 5 elements

7. Use the Periodic Table to determine which of the following elements has the highest energy valence electrons.

    (a) Sr
    (b) As
    (c) H
    (d) At
    (e) Na

8. Use the Periodic Table to determine which of the following elements has the lowest energy valence electrons.

    (a) Ga
    (b) B
    (c) Cs
    (d) Bi
    (e) Cl

9. Which energy level does the first row in the *d* sublevel block correspond to?

9.8: The Explanatory Power of the Quantum-Mechanical Model

9.9: Periodic Trends: Atomic Size, Ionization Energy, and Metallic Character

1. Why is the atomic size considered to have "no definite boundary"?
2. How is atomic size measured?

    (a) using a spectrophotomer
    (b) using a tiny ruler (called a nano ruler)
    (c) indirectly
    (d) directly

3. Draw a visual representation of the atomic radii of an iodine molecule.
4. Which of the following would be smaller?

    (a) In or Ga
    (b) K or Cs
    (c) Te or Po

5. Explain in your own words why Iodine is larger than Bromine.
6. What three factors determine the trend of atomic size going down a group?
7. What groups tend to show this trend?
8. Which of the following would have the largest atomic radii?

    (a) Si
    (b) C
    (c) Sn
    (d) Pb

9. Which of the following would have the smallest atomic radius?

    (a) $2s^2$
    (b) $4s^2 4p^3$
    (c) $2s^2 2p^4$
    (d) $4s^2$

10. Arrange the following in order of increasing atomic radii: Tl, B, Ga, Al, In.
11. Arrange the following in order of increasing atomic radii: Ge, Sn, C.
12. Which of the following would be larger?

    (a) Rb or Sn

    (b) Ca or As

13. Place the following in order of increasing atomic radii: Mg, Cl, S, Na.
14. Describe the atomic size trend for the rows in the Periodic Table.
15. Draw a visual representation of the periodic table describing the trend of atomic size.
16. Which of the following would have the largest atomic radii?

    (a) Sr

    (b) Sn

    (c) Rb

    (d) In

17. Which of the following would have the smallest atomic radii?

    (a) K

    (b) Kr

    (c) Ga

    (d) Ge

18. Place the following elements in order of increasing atomic radii: In, Ca, Mg, Sb, Xe.
19. Place the following elements in order of decreasing atomic radii: Al, Ge, Sr, Bi, Cs.
20. Knowing the trend for the rows, what would you predict to be the effect on the atomic radius if an atom were to gain an electron? Use an example in your explanation.
21. Knowing the trend for the rows, what would you predict to be the effect on the atomic radius if the atom were to lose an electron? Use an example in your explanation.

Ionization Energy

1. Define ionization energy and show an example ionization equation.
2. Draw a visual representation of the periodic table describing the trend of ionization energy.
3. Which of the following would have the largest ionization energy?

    (a) Na

    (b) Al

    (c) H

    (d) He

4. Which of the following would have the smallest ionization energy?

    (a) K

    (b) P

    (c) S

    (d) Ca

5. Place the following elements in order of increasing ionization energy: Na, O, Ca, Ne, K.
6. Place the following elements in order of decreasing ionization energy: N, Si, S, Mg, He.
7. Using experimental data, the first ionization energy for an element was found to be 600 kJ/mol. The second ionization energy for the ion formed was found to be 1,800 kJ/mol. The third ionization energy for the ion formed was found to be 2,700 kJ/mol. The fourth ionization energy for the ion formed was found to be 11,600 kJ/mol. And finally the fifth ionization energy was

found to be 15,000 kJ/mol. Write the reactions for the data represented in this question. To which group does this element belong? Explain.

8. Using electron configurations and your understanding of ionization energy, which would you predict would have higher second ionization energy: Na or Mg?
9. Comparing the first ionization energy (IE_1) of calcium, Ca, and magnesium, Mg, :

    (a) Ca has a higher IE_1 because its radius is smaller.

    (b) Mg has a higher IE_1 because its radius is smaller.

    (c) Ca has a higher IE_1 because its outer sub-shell is full.

    (d) Mg has a higher IE_1 because its outer sub-shell is full.

    (e) they have the same IE_1 because they have the same number of valence electrons.

10. Comparing the first ionization energy (IE_1) of beryllium, Be, and boron, B:

    (a) Be has a higher IE_1 because its radius is smaller.

    (b) B has a higher IE_1 because its radius is smaller.

    (c) Be has a higher IE_1 because its *s* sub-shell is full.

    (d) B has a higher IE_1 because its *s* sub-shell is full.

    (e) They have the same IE_1 because B has only one more electron than Be.

Electron Affinity

1. Define electron affinity and show an example equation.
2. Choose the element in each pair that has the lower electron affinity:

    (a) Li or N

    (b) Na or Cl

    (c) Ca or K

    (d) Mg or F

3. Why is the electron affinity for calcium much higher than that of potassium?
4. Draw a visual representation of the periodic table describing the trend of electron affinity.
5. Which of the following would have the largest electron affinity?

    (a) Se

    (b) F

    (c) Ne

    (d) Br

6. Which of the following would have the smallest electron affinity?

    (a) Na

    (b) Ne

    (c) Al

    (d) Rb

7. Place the following elements in order of increasing electron affinity: Te, Br, S, K, Ar.
8. Place the following elements in order of decreasing electron affinity: S, Sn, Pb, F, Cs.
9. Describe the trend that would occur for electron affinities for elements in Period 3. Are there any anomalies? Explain.
10. Comparing the electron affinity (EA) of sulfur, S, and phosphorus, P:

    (a) S has a higher EA because its radius is smaller.

    (b) P has a higher EA because its radius is smaller.

(c) S has a higher EA because its *p* sub-shell is half full.

(d) P has a higher EA because its *p* sub-shell is half full.

(e) they have the same EA because they are next to each other in the Periodic Table.

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CHAPTER OVERVIEW

12: Chemical Bonding

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: Bonding Models and AIDs Drugs
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: Resonance - Equivalent Lewis Structures for the Same Molecule
12.7: Predicting the Shapes of Molecules
12.8: Electronegativity and Polarity - Why Oil and Water Do not Mix

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12.1: Bonding Models and AIDs Drugs

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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:

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

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:

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

$$\mathbf{:}\ddot{\underset{\cdot\,\cdot}{\mathbf{Ne}}}\mathbf{:}$$

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:

$$\dot{A}\dot{l}:$$

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

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

EXERCISE 12.2.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a

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

Answer b

$$:\ddot{\underset{\cdot\,\cdot}{\mathbf{Ar}}}:$$

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:

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

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

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

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

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

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

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:

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

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

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



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:



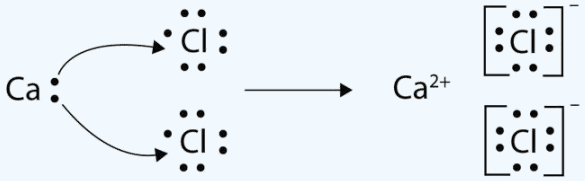
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the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

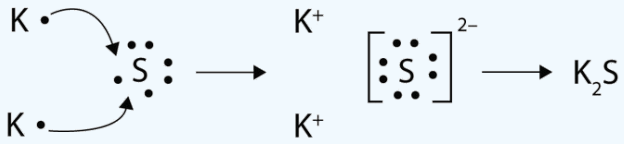


The oppositely charged ions attract each other to make $CaCl_2$.

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**.

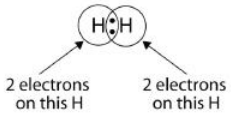
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

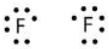
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



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

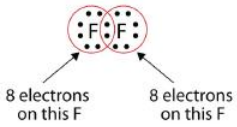
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



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:

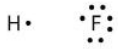


We can also write this using a dash to represent the shared electron pair:

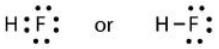


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three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

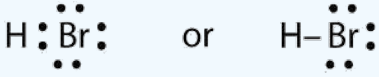
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

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 C_2H_4. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two C atoms} = 2 \times 4 = 8 \text{ valence electrons}$$

$$\text{four H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{total of 12 valence electrons in the molecule}$$

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:

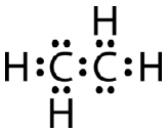


Figure 12.4.1: Incorrect dot structure of ethene. (CK12 License)

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.

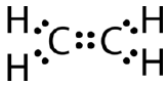


Figure 12.4.2: Correct dot structure for ethene. (CK12 License)

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.

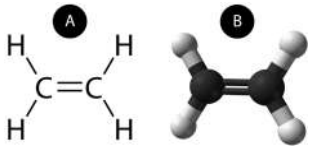


Figure 12.4.3: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4.

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.

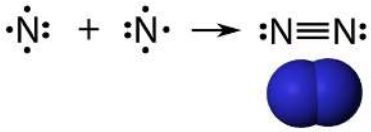


Figure 12.4.4: Triple bond in N_2.

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.

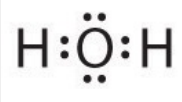
Example 12.5.1: Water

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.

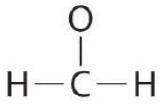
Steps for Writing Lewis Structures	Example 12.5.1
2. Arrange the atoms to show specific connections.	H O H Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning 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.

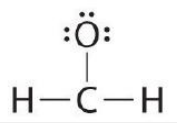
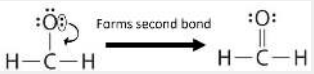
Example 12.5.2

Write the Lewis structure for the CH_2O molecule

Solution

Solutions to Example 10.4.2

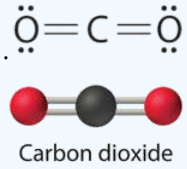
Steps for Writing Lewis Structures	Example 12.5.2
1. Determine the total number of valence electrons in the molecule or ion.	Each hydrogen atom (group 1) has 1 valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 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.

Steps for Writing Lewis Structures	Example 12.5.2
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

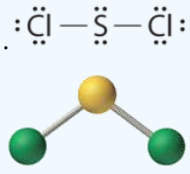
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer CO_2



Carbon dioxide

Answer SCl_2



Sulfur dichloride

The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

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, NH_4^+, is formed when a hydrogen ion $\left(H^+\right)$ attaches to the lone pair of an ammonia $\left(NH_3\right)$ molecule in a coordinate covalent bond.

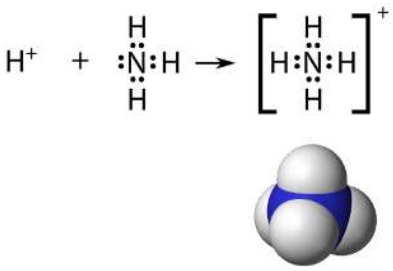


Figure 12.5.3: The ammonium ion. (CK12 License)

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:

$$1 \text{ N atom} = 5 \text{ valence electrons}$$

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

$$\text{subtract 1 electron for the } 1+ \text{ charge of the ion}$$

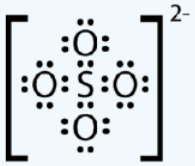
$$\text{total of 8 valence electrons in the ion}$$

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)

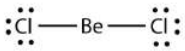
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

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:

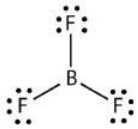


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

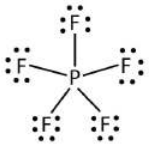
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting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

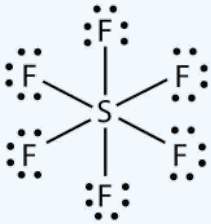
a. ClO
b. SF_6

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: 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 12.6.1. There are a total of 18 electrons in the structure and so the following two structures are possible.

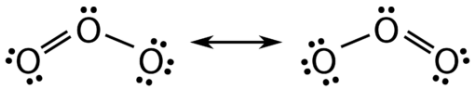


Figure 12.6.1: Resonance forms of ozone. Note the use of the double-headed arrow.

The structure on the left (12.6.1) 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 12.6.2).

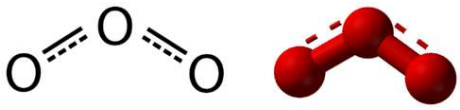


Figure 12.6.2: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure 12.6.1.

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 12.6.3.

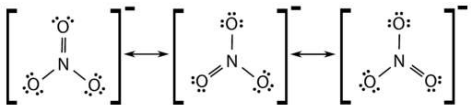


Figure 12.6.3: Resonance structure of nitrate anion.

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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12.7: 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 12.7.1: Beryllium hydride and carbon dioxide bonding.

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

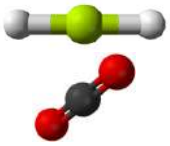


Figure 12.7.2: Beryllium hydride and carbon dioxide models. (CK12 Licence)

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:

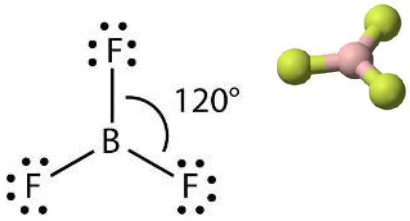


Figure 12.7.3: Boron trifluoride bonding. (CK12 Licence)

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:

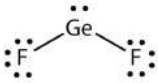


Figure 12.7.4: Germanium difluoride bonding.

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 12.7.1 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.

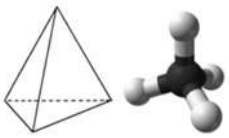


Figure 12.7.5: Tetrahedral structure of methane. (CK12 Licence)

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.

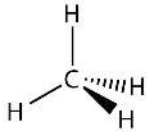


Figure 12.7.6: Methane bonding. (CK12 Licence)

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.

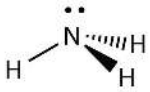


Figure 12.7.7: Ammonia bonding. (CK12 Licence)

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.

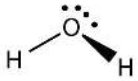


Figure 12.7.8: Water bonding.

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 12.7.9.



Figure 12.7.9: 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.

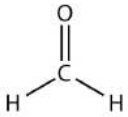


Figure 12.7.10: Formaldehyde bonding.

(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 12.7.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 12.7.1: 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 12.7.1

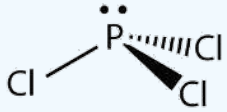
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

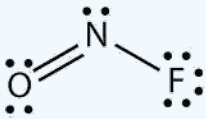
The first step is to draw the Lewis structure of the molecule.

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 12.7.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

EXERCISE 12.7.2

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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12.8: Electronegativity and Polarity - Why Oil and Water Do not 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 12.8.1.

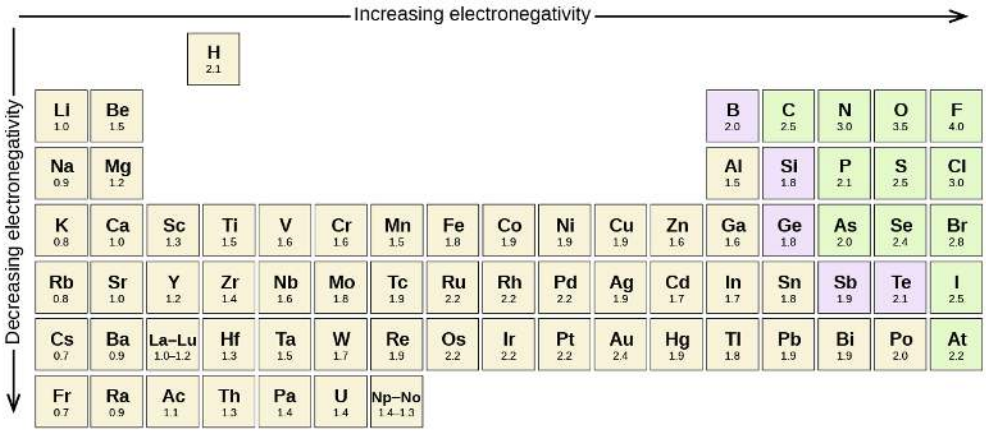


Figure 12.8.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

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.

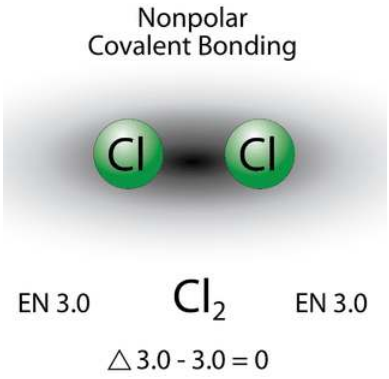


Figure 12.8.2: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

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

Polar Covalent Bonds

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

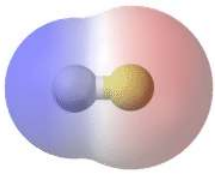


Figure 12.8.3: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

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

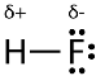


Figure 12.8.4: Use of δ to indicate partial charge.

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 12.8.5: 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 12.8.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure 12.8.1, 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 12.8.1

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 12.8.6: 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 $\left(\mathrm{CO}_2\right)$ 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.

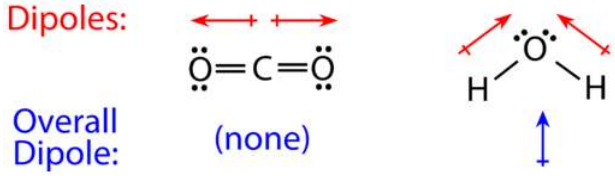


Figure 12.8.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

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 $\left(\mathrm{BF}_3\right)$ may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule $\left(\mathrm{NH}_3\right)$ is polar.

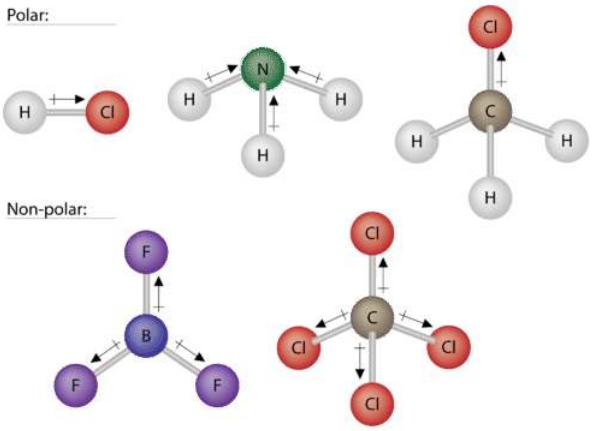


Figure 12.8.8: Some examples of polar and nonpolar molecules based on molecular geometry.

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 12.8.14). 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.

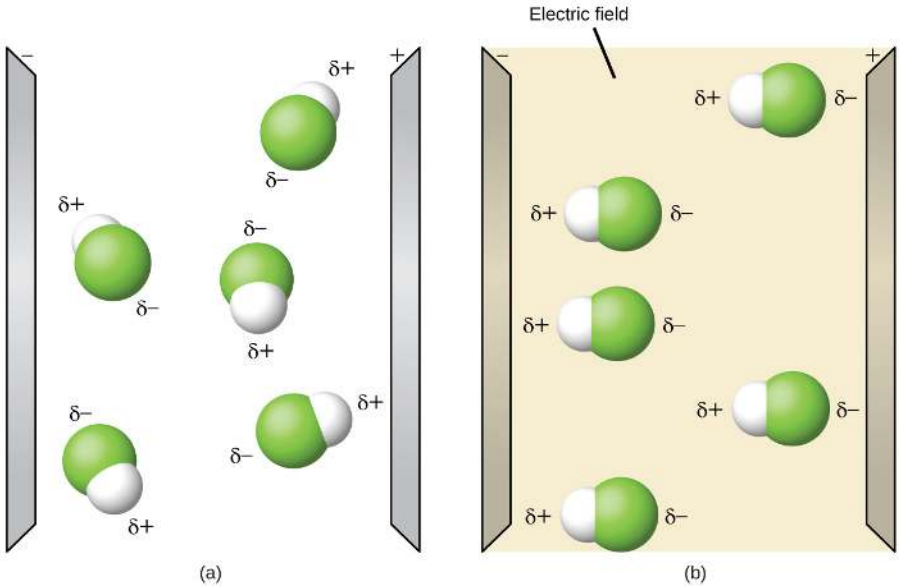


Figure 12.8.9: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

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 12.8.2:

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 $-\mathrm{OH}$ side is different from the other 3 $-\mathrm{H}$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

? Exercise 12.8.2

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

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: Boyle's Law - Pressure and Volume
13.5: Charles's Law- Volume and Temperature
13.6: The Combined Gas Law- Pressure, Volume, and Temperature
13.7: Avogadro's Law- Volume and Moles
13.8: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles
13.9: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen
13.10: Gay-Lussac's Law- Temperature and Pressure

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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).

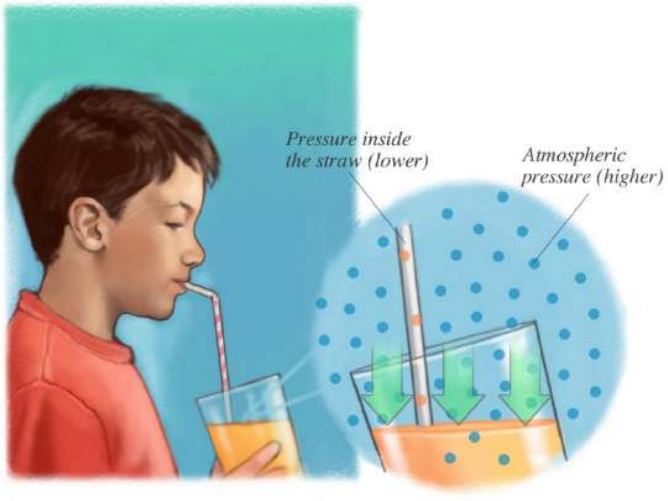


Figure 13.1.1: As you suck the air out of the straw, it creates a low pressure zone inside of it. With a low pressure zone, there is nothing pushing down on the juice, so it moves upward easily. (CC BY-NC 4.0; Ümit Kaya)

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.

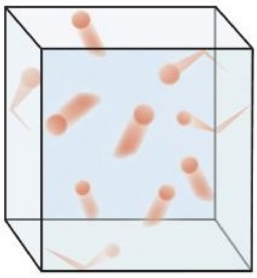


Figure 13.2.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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.	mmHg → atm $\frac{1\ atm}{760\ mmHg}$
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: 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 13.4.1 shows two representations of how Boyle's Law works.

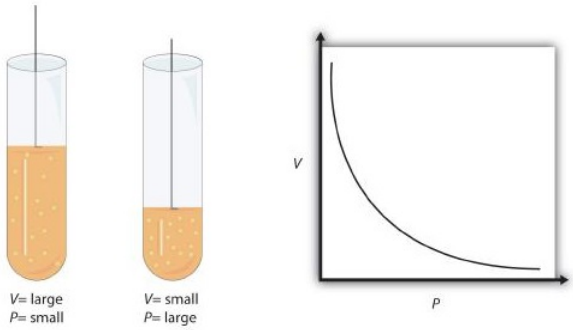


Figure 13.4.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot *P* versus *V* for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

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 13.4.1

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. $$V_2 = \frac{2.44 \ \cancel{atm} \times 4.01 \ \text{L}}{1.93 \ \cancel{atm}} = 5.07 \ \text{L}$$
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 13.4.1

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 13.4.2:

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.

Steps for Problem Solving	
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 13.4.2

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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13.5: 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.

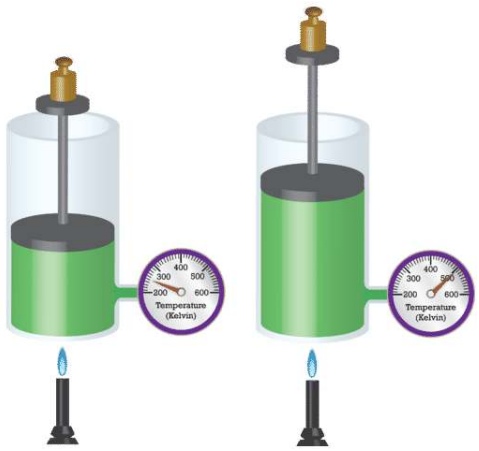


Figure 13.5.1: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

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 13.5.1: Temperature-Volume Data

Temperature (K)	**Volume** (mL)	$\boldsymbol{\frac{V}{T} = k}$ $\left(\frac{\mathrm{mL}}{\mathrm{K}}\right)$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in the figure below.

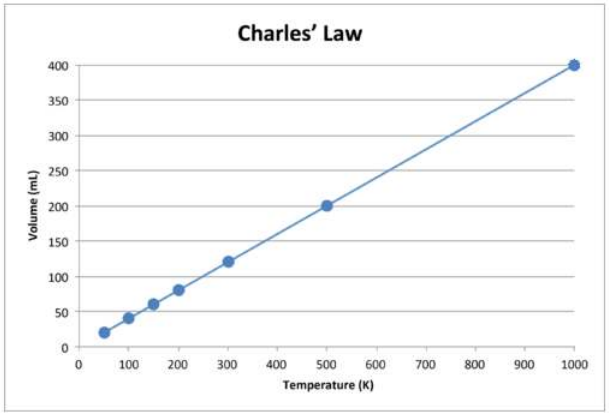


Figure 13.5.2:The volume of a gas increases as the Kelvin temperature increases.

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 13.5.1:

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: $V_1 = 2.20\ \mathrm{L}$ and $T_1 = 22^\circ\mathrm{C} = 295\ \mathrm{K}$ $T_2 = 71^\circ\mathrm{C} = 344\ \mathrm{K}$ Find: V_2 = ? L
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $V_2 = \frac{V_1 \times T_2}{T_1}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $V_2 = \frac{2.20\ \mathrm{L} \times 344\ \cancel{\mathrm{K}}}{295\ \cancel{\mathrm{K}}} = 2.57\ \mathrm{L}$

Steps for Problem Solving	
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

? Exercise 13.5.1

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 13.5.2:

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. $$T_2 = \frac{25.0 \cancel{\text{ L}} \times 206 \text{ K}}{34.8 \cancel{\text{ L}}} = 148 \text{ K}$$
Think about your result.	This is also equal to −125°C. As temperature decreases, volume decreases—which it does in this example.

? Exercise 13.5.2

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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13.6: 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 13.6.1:

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: P_2 = ? atm
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$P_2 = \frac{P_1V_1T_2}{T_1V_2}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$P_2 = \frac{(1.82\,atm)(8.33\ \cancel{L})(355\ \cancel{K})}{(286\ \cancel{K})(5.72\ \cancel{L})} = 3.22atm$$
Think about your result.	Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

Exercise 13.6.1

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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13.7: 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 13.7.1

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 13.7.1

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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13.8: 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: kPa, atm, or mm Hg. Therefore, R can have three different values.

We will demonstrate how R is calculated when the pressure is measured in kPa. The volume of $1.00\ \text{mol}$ of any gas at STP (Standard temperature, $273.15\ \text{K}$ and pressure, $1\ \text{atm}$) is measured to be $22.414\ \text{L}$ We can substitute $101.325\ \text{kPa}$ for pressure, $22.414\ \text{L}$ for volume, and $273.15\ \text{K}$ 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 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 13.8.1: 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 $\mathrm{J/K \cdot mol}$. A kilopascal multiplied by a liter is equal to the SI unit for energy, a joule (J).

Example 13.8.1 Oxygen Gas

What volume is occupied by $3.76\ \mathrm{g}$ of oxygen gas at a pressure of $88.4\ \mathrm{kPa}$ and a temperature of $19^{\circ}\mathrm{C}$? 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: • $P = 88.4\ \mathrm{kPa}$ • $T = 19^{\circ}\mathrm{C} = 292\ \mathrm{K}$ Mass $\mathrm{O_2} = 3.76\ \mathrm{g}$ Find: V = ? L
List other known quantities.	$\mathrm{O_2} = 32.00\ \mathrm{g/mol}$ $R = 8.314\ \mathrm{J/K \cdot mol}$
Plan the problem.	1. First, determine the number of moles of $\mathrm{O_2}$ from the given mass and the molar mass. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate.	1. $$3.76\ \cancel{\mathrm{g}} \times \frac{1\ \mathrm{mol\ O_2}}{32.00\ \cancel{\mathrm{g}}\ \mathrm{O_2}} = 0.1175\ \mathrm{mol\ O_2}$$ 2. Now substitute the known quantities into the equation and solve. $$V = \frac{nRT}{P} = \frac{0.1175\ \cancel{\mathrm{mol}} \times 8.314\ \mathrm{J/\cancel{K} \cdot}\ \cancel{\mathrm{mol}} \times 292\ \cancel{\mathrm{K}}}{88.4\ \cancel{\mathrm{kPa}}} = 3.23\ \mathrm{L}$$
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 $(22.4\ \mathrm{L/mol})$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 $(\mathrm{J}) = \mathrm{kPa \cdot L}$, the units cancel out correctly, leaving a volume in liters.

Example 13.8.2: 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

Steps for Problem Solving	
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 13.8.1

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 13.8.2

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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13.9: 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 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 atm, then the pressure of just the nitrogen in the air is 0.78 atm. The pressure of the oxygen in the air is 0.21 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 $P_{\text{total}} = 800 \text{ mm Hg}$.

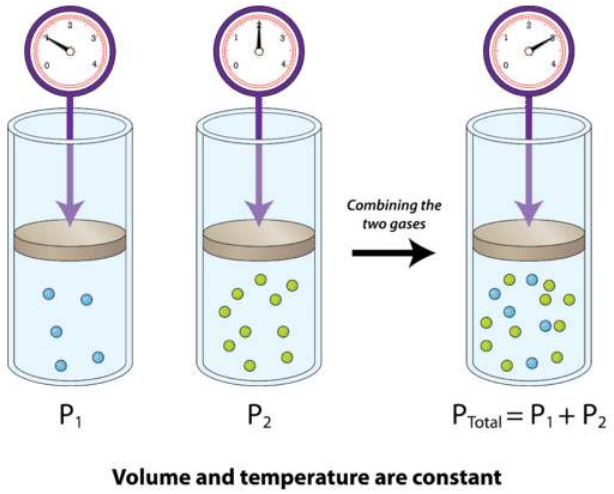


Figure 13.9.1: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

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 13.9.2). 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 13.9.2: 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 13.9.1: Vapor Pressure of Water (mm Hg) at Selected Temperatures $(^\circ\text{C})$

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 $2.58\ \text{L}$ of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is $98.60\ \text{kPa}$ Find the volume that the dry hydrogen would occupy at STP.

Solution

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

Known

- $V_{\text{Total}} = 2.58\ \text{L}$
- $T = 20^\circ\text{C} = 293\ \text{K}$
- $P_{\text{Total}} = 98.60\ \text{kPa} = 739.7\ \text{mm Hg}$

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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13.10: 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 13.10.1: Joseph Gay-Lussac.

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \quad \text{and} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

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 13.10.1

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

Solution

Solutions to Example 11.10.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $P_1 = 3.00\ \text{atm}$ $T_1 = 25^\circ\text{C} = 298\ \text{K}$ $T_2 = 845^\circ\text{C} = 1118\ \text{K}$ Find: $P_2 = ?\ \text{atm}$
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times T_2}{T_1}$$

Steps for Problem Solving	
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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CHAPTER OVERVIEW

14: Liquids, Solids, and Intermolecular Forces

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.

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: Interactions between Molecules
14.2: Properties of Liquids and Solids
14.3: Intermolecular Forces in Action- Surface Tension and Viscosity
14.4: Temperature Changes - Heat Capacity
14.5: Energy and Heat Capacity Calculations
14.6: Evaporation and Condensation
14.7: Melting, Freezing, and Sublimation
14.8: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole
14.9: Types of Crystalline Solids
14.10: Water - A Remarkable Molecule

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14.1: 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 $801^{\circ}\mathrm{C}$. 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 14.1.1: 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 $0^{\circ}\mathrm{C}$.

$$\mathrm{H_2O}\,(s) \rightleftharpoons \mathrm{H_2O}\,(l)$$

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 14.1.1: Melting Points of Common Materials

Materials	Melting Point (°C)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961

Materials	Melting Point (°C)
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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14.2: 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 14.2.1: 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 14.2.1. 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 14.2.2: 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.

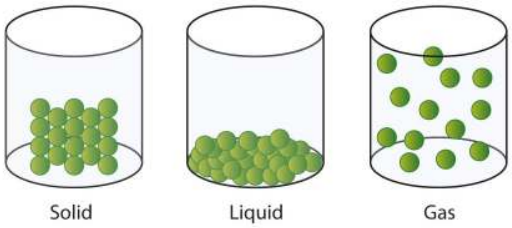


Figure 14.2.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

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 14.2.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 14.2.1 lists the different characteristics of these states.

Table 14.2.1: 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 14.2.1

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 14.2.1

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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14.3: Intermolecular Forces in Action- 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 14.3.1*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.

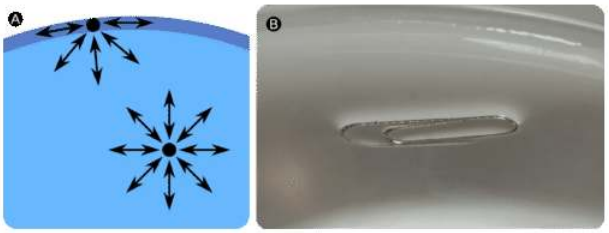


Figure 14.3.1: (A) Molecules at the surface of a liquid are pulled downwards into the liquid, creating a tightened surface. (B) Surface tension allows a paper clip to float on water's surface.

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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14.4: Temperature Changes - Heat Capacity

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends on both its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the wading pool.

Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$). Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $(\mathrm{J/g^{\circ}C})$ or calories per gram per degree $(\mathrm{cal/g^{\circ}C})$ (Table $14.4.1$). This text will use $\mathrm{J/g^{\circ}C}$ for specific heat.

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

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

Table 14.4.1: Specific Heat Capacities

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

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



Figure 14.4.1: 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.

Summary

- Heat capacity is the amount of heat required to raise the temperature of an object by $1^{o}C$).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{o}C$.

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14.5: Energy and Heat Capacity Calculations

Learning Objectives

- To relate heat transfer to temperature change.

Heat is a familiar manifestation of transferring energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat (q) to specific heat (c_p), mass (m), and temperature change (ΔT) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature.

Every substance has a characteristic specific heat, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express Δ*T*. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°. Table $14.5.1$ lists the specific heats for various materials.

Table 14.5.1*: Specific Heats of Some Common Substances*

Substance	**Specific Heat** $(\mathrm{J/g^oC})$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

The *direction* of heat flow is not shown in heat = *mc*Δ*T*. If energy goes into an object, the total energy of the object increases, and the values of heat Δ*T* are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and Δ*T* are negative.

Example 14.5.1

A 15.0 g piece of cadmium metal absorbs 134 J of heat while rising from 24.0°C to 62.7°C. Calculate the specific heat of cadmium.

Solution

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

Known

- Heat = $q = 134$ J
- Mass = $m = 15.0$ g
- $\Delta T = 62.7^{\circ}\text{C} - 24.0^{\circ}\text{C} = 38.7^{\circ}\text{C}$

Unknown

- c_p of cadmium =? $\text{J/g}^{\circ}\text{C}$

The specific heat equation can be rearranged to solve for the specific heat.

Step 2: Solve.

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7^{\circ}\text{C}} = 0.231\ \text{J/g}^{\circ}\text{C}$$

Step 3: Think about your result.

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known (Table 14.5.1), they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that a 60.0 g of water at 23.52°C was cooled by the removal of 813 J of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g}^{\circ}\text{C} \times 60.0\ \text{g}} = 3.24^{\circ}\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^{\circ}\text{C} - 3.24^{\circ}\text{C} = 20.28^{\circ}\text{C}$$

Example 14.5.2

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

Solution

We can use heat = $mc\Delta T$ to determine the amount of heat, but first we need to determine ΔT. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 73.3^{\circ}\text{C} - 25.0^{\circ}\text{C} = 48.3^{\circ}\text{C}$$

The mass is given as 150.0 g, and Table 7.3 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into heat = $mc\Delta T$ and solve for amount of heat:

$$\text{heat} = (150.0\ \text{g})\left(0.108\ \frac{\text{cal}}{\text{g} \cdot {}^{\circ}\text{C}}\right)(48.3^{\circ}\text{C}) = 782\ \text{cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

Exercise 14.5.1

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

Answer

Heat leaves the aluminum block.

Example 14.5.2

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 14.5.1?

Solution

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0°\text{C} - 97.5°\text{C} = -75.5°\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, −71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for c:

$$-71.7 \text{ cal} = (10.3 \text{ g})(c)(-75.5°\text{C})$$

$$c = \frac{-71.7 \text{ cal}}{(10.3 \text{ g})(-75.5°\text{C})}$$

$$c = 0.0923 \text{ cal/g•°C}$$

This value for specific heat is very close to that given for copper in Table 7.3.

Exercise 14.5.2

A 10.7 g crystal of sodium chloride (NaCl) has an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

Answer

Summary

Specific heat calculations are illustrated.

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14.6: 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 14.6.1: 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.

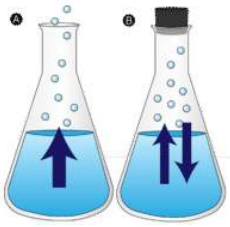


Figure 14.6.2: Evaporation (A) and condensation (B).

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).

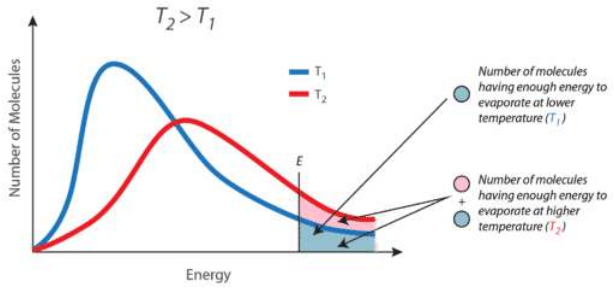


Figure 14.6.3: Kinetic energy distribution curves for a liquid at two temperatures T_1 and T_2. The shaded area represents the molecules with enough kinetic energy to escape the liquid and become vapor.

At 29,029 feet $(8848\ \text{m})$, 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.

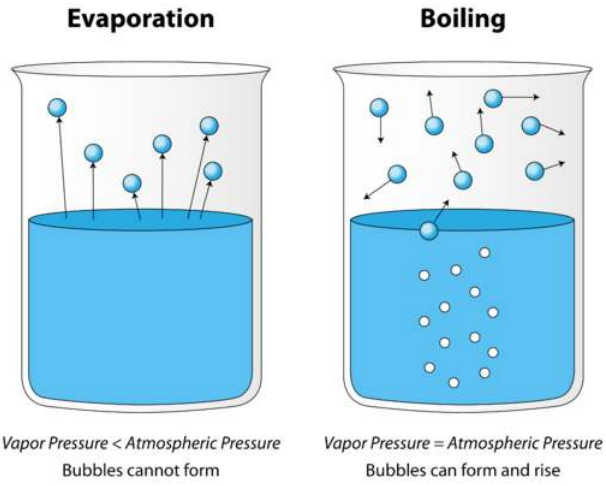


Figure 14.6.4: Comparison between evaporation and boiling.

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 $760\ \text{mm Hg}$ (or $1\ \text{atm}$ or $101.3\ \text{kPa}$).

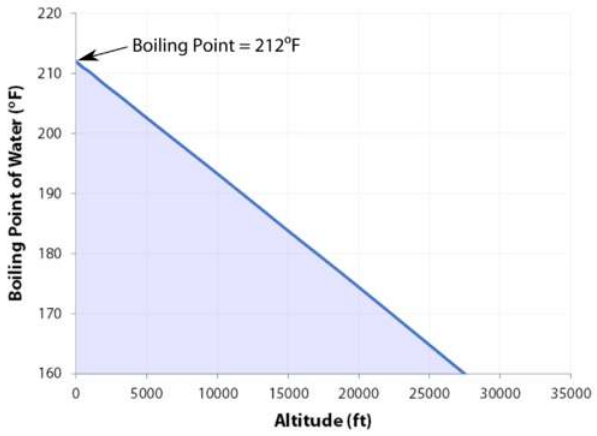


Figure 14.6.5: Influence of altitude on the boiling point of water.

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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14.7: 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 14.7.1).



Figure 14.7.1: 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:

$$\text{heat} = n \times \Delta H_{fus} \tag{14.7.1}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{fus} \tag{14.7.2}$$

where m is the mass in grams and ΔH_{fus} is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap} \tag{14.7.3}$$

where n is the number of moles) and ΔH_{vap} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{vap} \tag{14.7.4}$$

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 14.7.1

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. 14.7.1b) 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 14.7.1

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 14.7.1 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 14.7.1: 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:

$$\text{solid} \rightarrow \text{gas} \tag{14.7.5}$$

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:

$$CO_2(s) \xrightarrow{-78.5^\circ C} CO_2(g) \tag{14.7.6}$$

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 (NaCl) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at $801^{\circ}\mathrm{C}$. Ice (solid $\mathrm{H_2O}$) 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 $0^{\circ}\mathrm{C}$.

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 $0^{\circ}\mathrm{C}$.

$$\mathrm{H_2O}\,(s) \rightleftharpoons \mathrm{H_2O}\,(l)$$

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 14.7.2: 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 14.7.2

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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14.8: 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 14.8.1*a*.

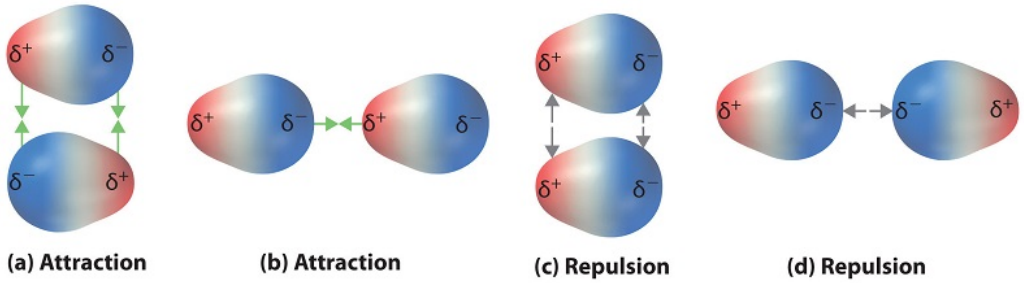


Figure 14.8.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or 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 14.8.1*c*). Hence dipole–dipole interactions, such as those in Figure 14.8.1*b*, are *attractive intermolecular interactions*, whereas those in Figure 14.8.1*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 14.8.2. On average, however, the attractive interactions dominate.

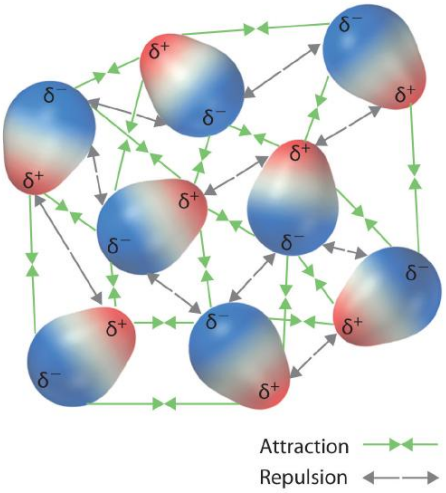


Figure 14.8.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

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 14.8.1.

Table 14.8.1: 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

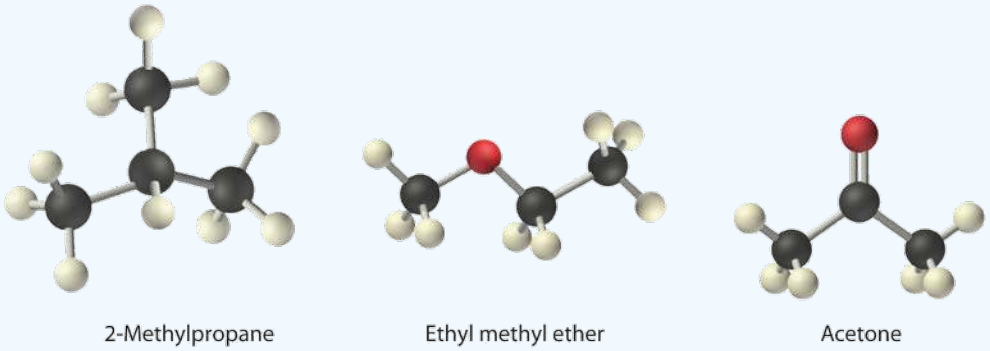
> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*



Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

EXAMPLE 14.8.1

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 14.8.1

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 14.8.2).

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 14.8.2: 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 14.8.3, 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.

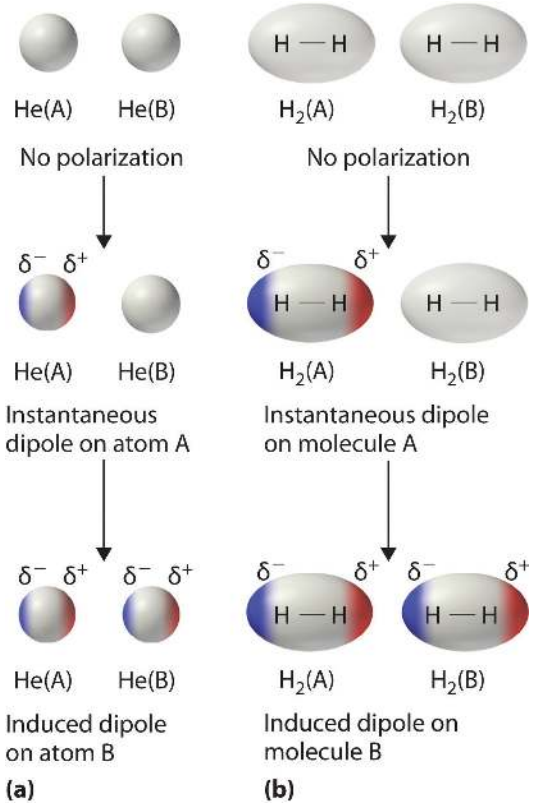


Figure 14.8.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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 14.8.3, tends to become more pronounced as atomic and molecular masses increase (Table 14.8.2). 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 14.8.4). 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 14.8.4 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).

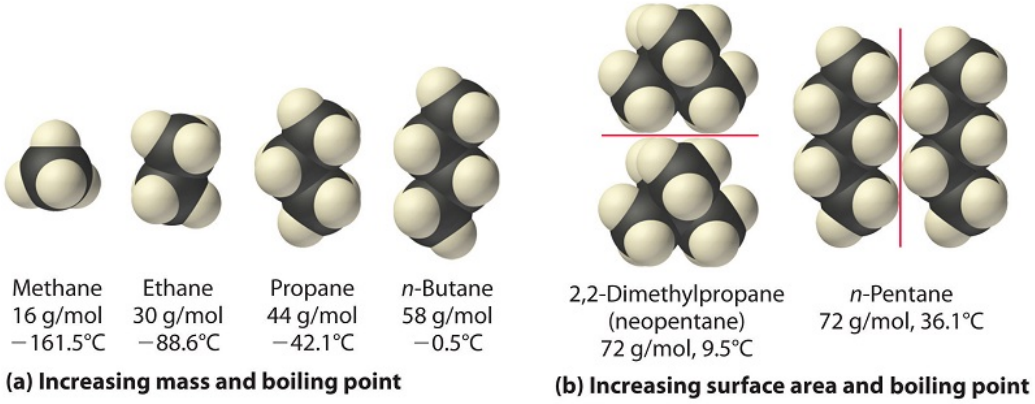


Figure 14.8.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger 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 14.8.2

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 14.8.2

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 14.8.5. 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.

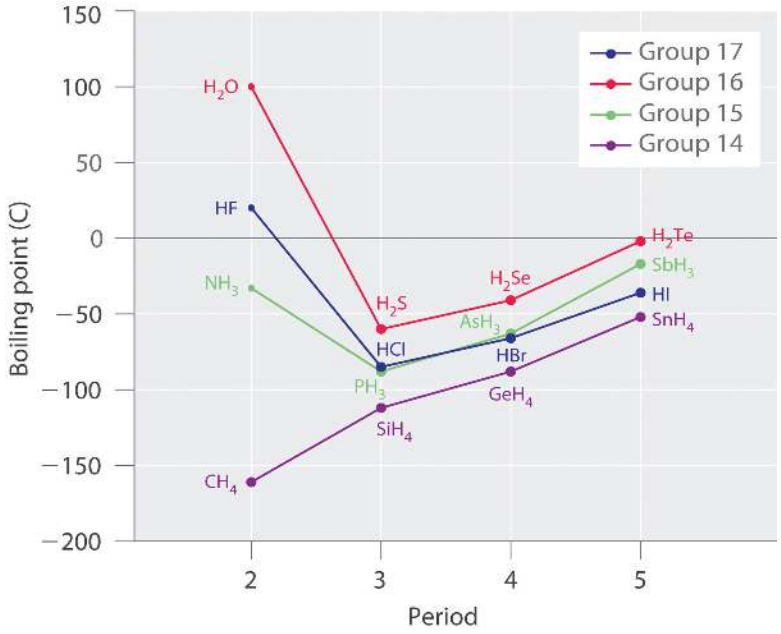


Figure 14.8.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously 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 14.8.6. 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.

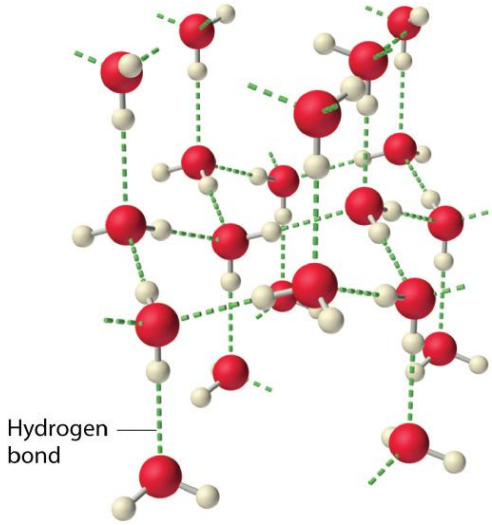


Figure 14.8.6: The Hydrogen-Bonded Structure of Ice

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 14.8.3

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:

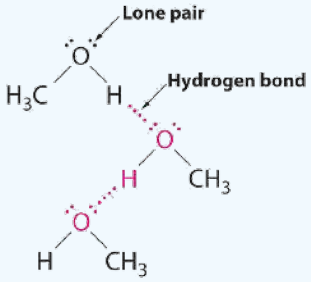
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

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:



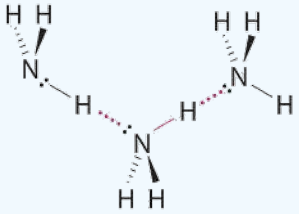
Hydrogen bonding in methanol

EXERCISE 14.8.3

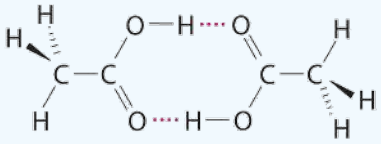
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

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 14.8.4: 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 14.8.4

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 14.8.5

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 14.8.6

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.

14.8: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by LibreTexts.

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14.9: Types of Crystalline Solids

Learning Objectives

- Identify different types of solid substances.

As a society, we sometimes take things for granted. For example, it is often assumed that we will get electric power when we connect a plug to an electrical outlet. The wire that comprises that outlet is almost always copper, a material that conducts electricity well. The unique properties of the solid copper allow electrons to flow freely through the wire and into whatever device we connect it to. Then we can enjoy music, television, computer work, or whatever other activity we want to undertake. However, these activities—and the miracle of electricity itself—would not be possible without that copper wire!

Classes of Crystalline Solids

Crystalline substances can be described by the types of particles in them and the types of chemical bonding that take place between the particles. There are four types of crystals: (1) **ionic**, (2) **metallic**, (3) **covalent network**, and (4) **molecular**. Properties and several examples of each type are listed in the following table and are described in the table below.

Table 14.9.1: Crystalline Solids: Melting and Boiling Points

Type of Crystalline Solid	Examples (formulas)	Melting Point (°C)	Normal Boiling Point (°C)
Ionic	NaCl	801	1413
	CaF_2	1418	1533
Metallic	Hg	-39	630
	Na	371	883
	Au	1064	2856
	W	3410	5660
Covalent Network	B	2076	3927
	C (diamond)	3500	3930
	SiO_2	1600	2230
Molecular	H_2	-259	-253
	I_2	114	184
	NH_3	-78	-33
	H_2O	0	100

Ionic crystals - The ionic crystal structure consists of alternating positively-charged cations and negatively-charged anions (see figure below). The ions may either be monatomic or polyatomic. Generally, ionic crystals form from a combination of Group 1 or 2 metals and Group 16 or 17 nonmetals or nonmetallic polyatomic ions. Ionic crystals are hard and brittle and have high melting points. Ionic compounds do not conduct electricity as solids, but do conduct electricity when molten or in aqueous solution.

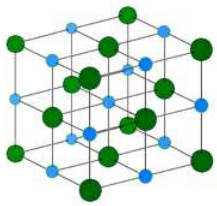


Figure 14.9.1: NaCl crystal.

Metallic crystal - Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons (see figure below). These electrons, also referred to as delocalized electrons, do not belong to any one atom, but are capable of moving through the entire crystal. As a result, metals are good conductors of electricity. As seen in the table above, the melting points of metallic crystals span a wide range.

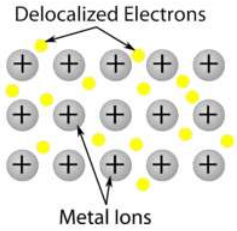


Figure 14.9.2: Metallic crystal lattice with free electrons able to move among positive metal atoms.

Covalent network crystals - A covalent network crystal consists of atoms at the lattice points of the crystal, with each atom being covalently bonded to its nearest neighbor atoms (see figure below). The covalently bonded network is three-dimensional and contains a very large number of atoms. Network solids include diamond, quartz, many metalloids, and oxides of transition metals and metalloids. Network solids are hard and brittle, with extremely high melting and boiling points. Being composed of atoms rather than ions, they do not conduct electricity in any state.

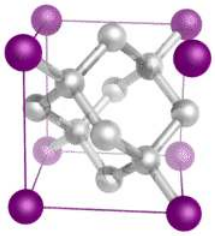


Figure 14.9.3: Diamond is a network solid and consists of carbon atoms covalently bonded to one another in a repeating three-dimensional pattern. Each carbon atom makes for single covalent bonds in a tetrahedral geometry.

Molecular crystals - Molecular crystals typically consist of molecules at the lattice points of the crystal, held together by relatively weak intermolecular forces (see figure below). The intermolecular forces may be dispersion forces in the case of nonpolar crystals, or dipole-dipole forces in the case of polar crystals. Some molecular crystals, such as ice, have molecules held together by hydrogen bonds. When one of the noble gases is cooled and solidified, the lattice points are individual atoms rather than molecules. In all cases, the intermolecular forces holding the particles together are far weaker than either ionic or covalent bonds. As a result, the melting and boiling points of molecular crystals are much lower. Lacking ions or free electrons, molecular crystals are poor electrical conductors.

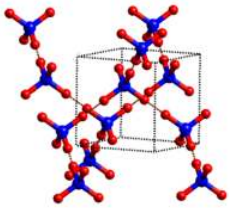


Figure 14.9.4: Ice crystal structure.

Some general properties of the four major classes of solids are summarized in Table 14.9.2

Table 14.9.2: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

Example 14.9.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A. **Germanium** lies in the p block just under Si, along the diagonal line of semi-metallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a **covalent solid**.

RbI contains a metal from group 1 and a nonmetal from group 17, so it is **an ionic solid** containing Rb^+ and I^- ions.

The compound $C_6(CH_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form **a molecular solid** with no covalent bonds between them.

Zn is a d-block element, so it is **a metallic solid**.

B. Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is

$$C_6(CH_3)_6 < Zn < RbI < Ge.$$

The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

Exercise 14.9.1

Classify CO_2, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer

CO_2 (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent).

The actual melting points are: CO_2, about -15.6°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

- Ionic crystals are composed of alternating positive and negative ions.
- Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons.
- Covalent crystals are composed of atoms which are covalently bonded to one another.
- Molecular crystals are held together by weak intermolecular forces.

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14.10: Water - A Remarkable Molecule

Learning Objectives

- Interpret the unique properties of water in terms of a phase diagram.

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?

Phase Diagram for Water

Water is a unique substance in many ways. One of these special properties is the fact that solid water (ice) is less dense than liquid water just above the freezing point. The phase diagram for water is shown in the figure below.

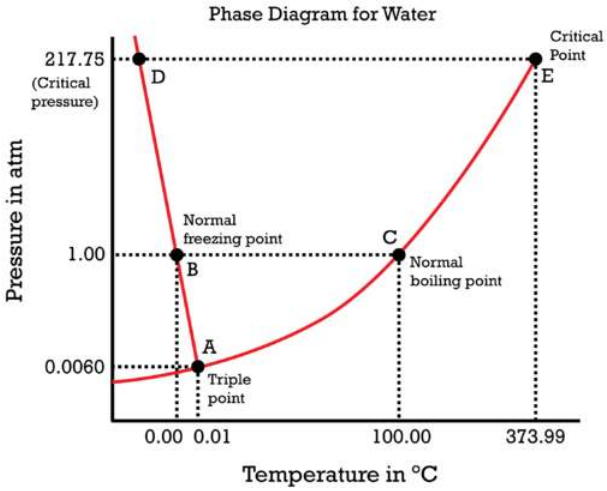


Figure 14.10.1: Phase diagram for water.

Notice one key difference between the general phase diagram and the phase diagram for water. In water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason for this is that water is an unusual substance, as its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

Refer again to water's phase diagram (figure above). Notice point E, labeled the **critical point**. What does that mean? At 373.99°C, particles of water in the gas phase are moving very, very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas. The **critical pressure** (P_{C}) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid. For water, the critical pressure is very high, $217.75\ \text{atm}$ The critical point is the intersection point of the **critical temperature** and the critical pressure.

Summary

- Solid water is less dense than liquid water just above the freezing point.
- The critical temperature (T_C) of a substance is the highest temperature at which the substance can possibly exist as a liquid.
- The critical pressure (P_C) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid.
- The critical point is the intersection point of the critical temperature and the critical pressure.

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CHAPTER OVERVIEW

15: SOLUTIONS

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.

15.1: Tragedy in Cameroon
15.2: Solutions - Homogeneous Mixtures
15.3: Solutions of Solids Dissolved in Water- How to Make Rock Candy
15.4: Solutions of Gases in Water
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15.1: TRAGEDY IN CAMEROON

Lake Nyos is a deep crater lake in the Northwest region of Cameroon, high on the flank of an inactive volcano in the Oku volcanic plain along the Cameroon line of volcanic activity. A volcanic dam impounds the lake waters. A pocket of magma lies beneath the lake and leaks carbon dioxide (CO_2) into the water, changing it into carbonic acid. Nyos is one of only three known exploding lakes to be saturated with carbon dioxide in this way.

In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 15.1.1), a deep lake in a volcanic crater. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a) (b)

Figure 15.1.1: Two photos are shown. The first is an aerial view of a lake surrounded by green hills. The second shows a large body of water with a fountain sending liquid up into the air several yards or meters above the surface of the water. (a) It is believed that the 1986 disaster, that killed more than 1700 people near Lake Nyos in Cameroon, resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (Credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans.)

Following the Lake Nyos tragedy, scientists investigated other African lakes to see if a similar phenomenon could happen elsewhere. Lake Kivu in Democratic Republic of Congo, 2,000 times larger than Lake Nyos, was also found to be supersaturated, and geologists found evidence for out-gassing events around the lake about every one thousand years.

CONTRIBUTIONS & ATTRIBUTIONS

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

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15.2: 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 15.2.1: 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 NaCl in liquid water, while air is a solution of a gaseous solute ($\mathrm{O_2}$) in a gaseous solvent ($\mathrm{N_2}$). In all cases, however, the overall phase of the solution is the same phase as the solvent. Table 15.2.1 lists some common types of solutions, with examples of each.

Table 15.2.1: Types of Solutions

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

EXAMPLE 15.2.1: SUGAR AND WATER

A solution is made by dissolving 1.00 g of sucrose ($\mathrm{C_{12}H_{22}O_{11}}$) 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 15.2.1

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, 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 15.2.2: 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 15.2.2: Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

✔ EXAMPLE 15.2.2: POLAR AND NONPOLAR SOLVENTS

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

EXERCISE 15.2.2

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

Answer

H_2O, because both experience hydrogen bonding.

EXAMPLE 15.2.3

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol (CH_3OH)
b. sodium sulfate (\ce{Na2SO4}\))
c. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

a. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
b. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
c. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

EXERCISE 15.2.3: TOLUENE

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

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

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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15.3: 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 $15.3.1$ 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 15.3.1: 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.

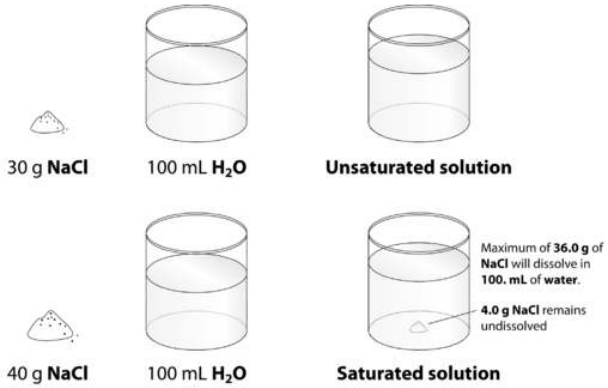


Figure 15.3.1: When 30.0 g of NaCl is added to 100 mL, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution.

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 15.3.1).

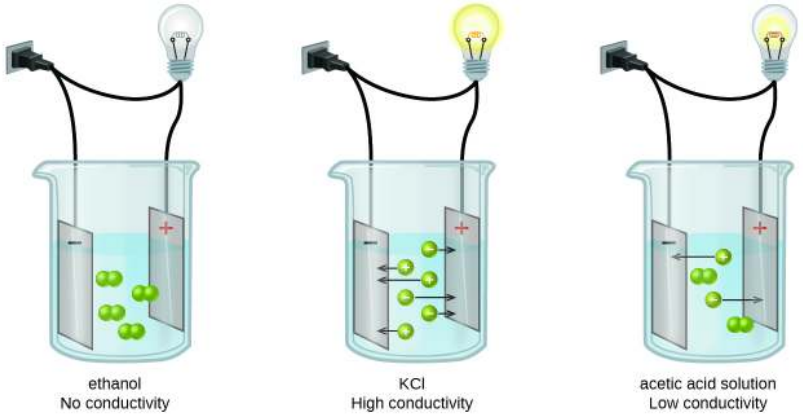


Figure 15.3.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram 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 15.3.2 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.

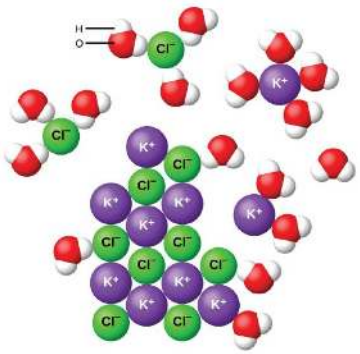


Figure 15.3.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight 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 15.3.1: 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 15.3.1

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 $20^{\circ}C$. 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 15.3.4).

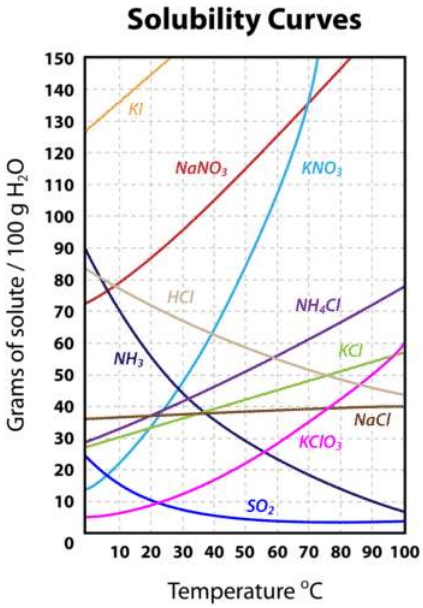


Figure 15.3.4: Solubility curves for several compounds.

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^oC. According to the solubility curve, approximately 48 g of KNO_3 will dissolve at 30^oC. 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^oC. According to the curve, the solubility of KNO_3 at 60^oC 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^oC. The solubility at 0^oC 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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15.4: 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 15.4.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

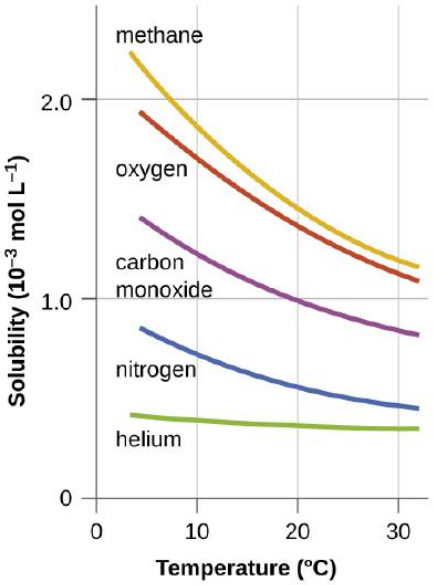


Figure 15.4.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

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 15.4.2).



(a) (b)

Figure 15.4.2: (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 15.4.3). 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."

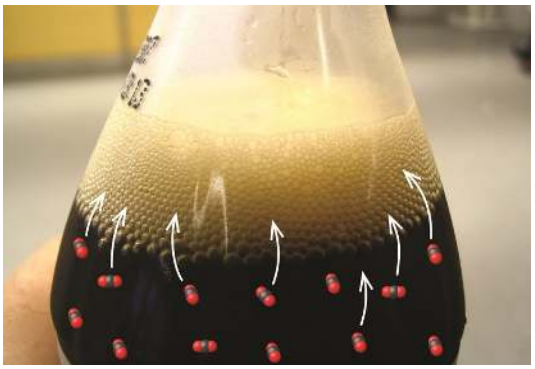


Figure 15.4.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. A dark brown liquid is shown in a clear, colorless 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:

$$\mathrm{H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)}$$

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 15.4.1: 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*.

$$C_g = kP_g$$

$$k = \frac{C_g}{P_g}$$

$$= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}}$$

$$= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1}$$

$$(1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1})$$

Now we can use *k* to find the solubility at the lower pressure.

$$C_g = kP_g$$

$$1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa}$$

$$(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr})$$

$$= 2.82 \times 10^{-4}\ \text{mol L}^{-1}$$

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 15.4.1

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")

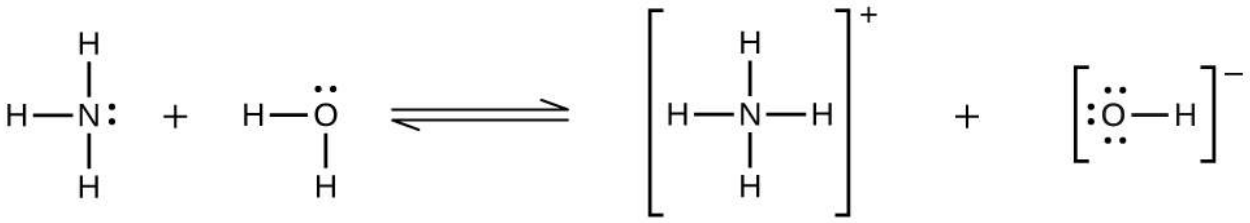
Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing 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 15.4.4).



Figure 15.4.4: (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.

CONTRIBUTIONS & ATTRIBUTIONS

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

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15.5: Specifying 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.

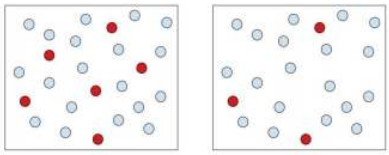


Figure 15.5.1: The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 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 15.5.1

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 15.5.1

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 gof a 5.00% solution of sodium chloride, the mass of solute needs to be determined.

Solution

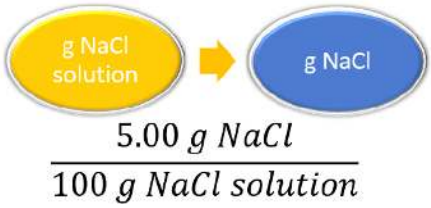
Given: 3000.0 g NaCl solution

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:



To solve for the mass of NaCl, the given mass of solution is multiplied by the conversion factor.

$$gNaCl = 3,000.0\ g\ NaCl\ \cancel{solution} \times \frac{5.00\ g\ NaCl}{100\ g\ NaCl\ \cancel{solution}} = 150.0 g\ NaCl$$

You would need to weigh out 150 g of NaCl and add it to 2850 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 15.5.1

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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15.6: Specifying 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.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{15.6.1}$$

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 $\left[\text{Ag}^+\right]$ 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):

$$22.4 \ \cancel{gHCl} \times \frac{1 \ mol \ HCl}{36.5 \ \cancel{gHCl}} = 0.614 \, mol \ HCl$$

Step 2: Now we can use the definition of molarity to determine a concentration:

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

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.

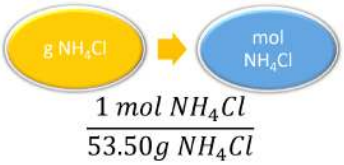
Example 15.6.1

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 $= 42.23$ g NH_4Cl Volume solution $= 500.0$ mL $= 0.5000$ L Find: Molarity = ? M
List other known quantities.	Molar mass $\text{NH}_4\text{Cl} = 53.50$ g/mol

Steps for Problem Solving	
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. $\mathrm{M} = \frac{\mathrm{mol\ NH_4Cl}}{\mathrm{L\ solution}}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $42.23\ \cancel{\mathrm{g\ NH_4Cl}} \times \frac{1\ \mathrm{mol\ NH_4Cl}}{53.50\ \cancel{\mathrm{g\ NH_4Cl}}} = 0.7893\ \mathrm{mol\ NH_4Cl}$ $\frac{0.7893\ \mathrm{mol\ NH_4Cl}}{0.5000\ \mathrm{L\ solution}} = 1.579\ \mathrm{M}$
Think about your result.	The molarity is $1.579\ \mathrm{M}$, meaning that a liter of the solution would contain $1.579\ \mathrm{mol\ NH_4Cl}$. Four significant figures are appropriate.

? Exercise 15.6.1A

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 15.6.1B

What is the concentration, in $\mathrm{mol/L}$, where $137\ \mathrm{g}$ of NaCl has been dissolved in enough water to make $500\ \mathrm{mL}$ of solution?

Answer

4.69 M NaCl

Using Molarity in Calculations

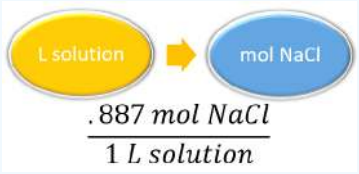
Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of 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 15.6.2: 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.

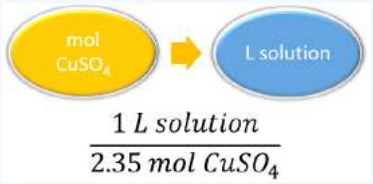
Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 15.6.3: 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:



$$4.88\ mol\ CuSO_4 \times \frac{1\ L\ solution}{2.35\ mol\ CuSO_4} = 2.08\ L\ of\ solution$$

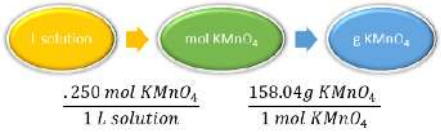
In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams. The following example illustrates this.

Example 15.6.4

A chemist needs to prepare 3.00 L of a 0.250 M solution of potassium permanganate $\left(KMnO_4\right)$. 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 M Volume = 3.00 L Find: Mass $KMnO_4$ =? g
List other known quantities.	Molar mass $KMnO_4$ = 158.04 g/mol 0.250 mol $KMnO_4$ to 1 L of $KMnO_4$ solution
Plan the problem.	
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $\text{mol KMnO}_4 = 0.250\ \text{M KMnO}_4 \times 3.00\ \text{L} = 0.750\ \text{mol}$ $3.00\ L\ solution \times \frac{0.250\ \text{mol KMnO}_4}{1\ L\ solution} \times \frac{158.04\ \text{g KMnO}_4}{1\ \text{mol KMnO}_4} = 119\ \text{g KM}$
Think about your result.	When 119 g of potassium permanganate is dissolved into water to make 3.00 L of solution, the molarity is 0.250 M.

Exercise 15.6.4A

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 15.6.4B

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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15.7: 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.

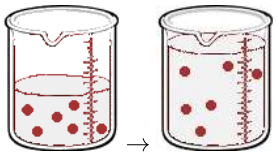
STOCK SOLUTIONS

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

$$\boxed{M_1V_1 = M_2V_2} \tag{15.7.1}$$

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 15.7.1: DILUTING NITRIC ACID

Nitric acid $\left(\text{HNO}_3\right)$ 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 $\text{HNO}_3\,(V_1) = ?\ \text{L}$
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. $V_1 = \frac{0.50\ \text{M} \times 8.00\ \text{L}}{16\ \text{M}} = 0.25\ \text{L}$ (15.7.2)
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 M to 0.5 M.

EXERCISE 15.7.1

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

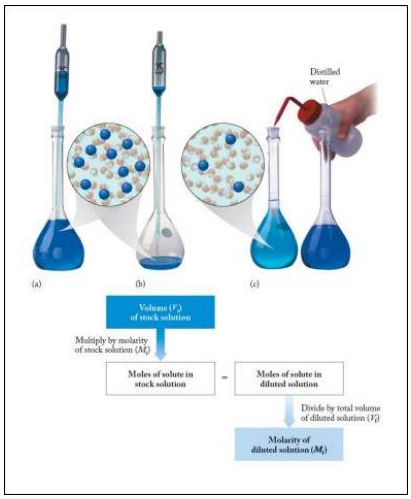
Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).

DILUTING AND MIXING SOLUTIONS

Diluting and Mixing Solutions



How to Dilute a Solution by CarolinaBiological



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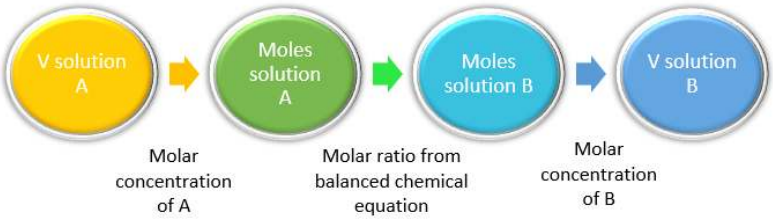
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15.8: SOLUTION STOICHIOMETRY

LEARNING OBJECTIVES

- Determine amounts of reactants or products in aqueous solutions.

As we learned previously, double replacement reactions involve the reaction between ionic compounds in solution and, in the course of the reaction, the ions in the two reacting compounds are "switched" (they *replace* each other). Because these reactions occur in aqueous solution, we can use the concept of molarity to directly calculate the number of moles of reactants or products that will be formed, and therefore their amounts (i.e. volume of solutions or mass of precipitates).



As an example, lead (II) nitrate and sodium chloride react to form sodium nitrate and the *insoluble* compound, lead (II) chloride.

$$\mathrm{Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow PbCl_2(s) + 2\,NaNO_3(aq)} \tag{15.8.1}$$

In the reaction shown above, if we mixed 0.123 L of a 1.00 M solution of NaCl with 1.50 M solution of $\mathrm{Pb(NO_3)_2}$, we could calculate the volume of $\mathrm{Pb(NO_3)_2}$ solution needed to completely precipitate the $\mathrm{Pb^{2+}}$ ions.

The molar concentration can also be expressed as the following:

$$1.00\,M\,\mathrm{NaCl} = \frac{1.00\ mol\ \mathrm{NaCl}}{1\ L\ \mathrm{NaCl\ solution}}$$

and

$$1.50\,M\,\mathrm{Pb(NO_3)_2} = \frac{1.50\ mol\ \mathrm{Pb(NO_3)_2}}{1\ L\ \mathrm{Pb(NO_3)_2 solution}}$$

First, we must examine the reaction stoichiometry in the balanced reaction (Equation 15.8.1). In this reaction, one mole of $\mathrm{Pb(NO_3)_2}$ reacts with two moles of NaCl to give one mole of $\mathrm{PbCl_2}$ precipitate. Thus, the concept map utilizing the stoichiometric ratios is:



so the volume of lead (II) nitrate that reacted is calculated as:

$$0.123\ L\ \mathrm{NaCl solution} \times \frac{1.00\ mol\ \mathrm{NaCl}}{1\ L\ \mathrm{NaCl\ solution}} \times \frac{1\ mol\ \mathrm{Pb(NO_3)_2}}{2\ mol\ \mathrm{NaCl}} \times \frac{1\ L\ \mathrm{Pb(NO_3)_2\ solution}}{1.5\ mol\ \mathrm{Pb(NO_3)_2}} = 0.041\ \mathrm{Pb(NO_3)_2}$$
$$L\ \mathrm{solution}$$

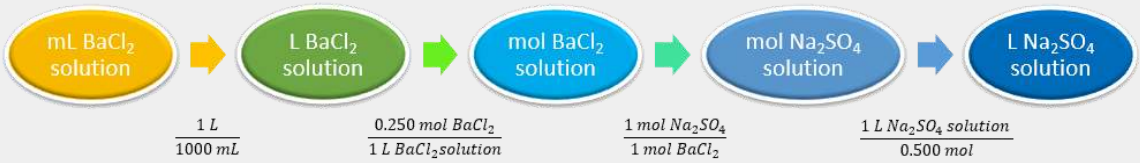
This volume makes intuitive sense for two reasons: (1) the number of moles of $\mathrm{Pb(NO_3)_2}$ required is half of the number of moles of NaCl, based off of the stoichiometry in the balanced reaction (Equation 15.8.1); (2) the concentration of $\mathrm{Pb(NO_3)_2}$ solution is 50% greater than the NaCl solution, so less volume is needed.

EXAMPLE 15.8.1

What volume (in L) of 0.500 M sodium sulfate will react with 275 mL of 0.250 M barium chloride to completely precipitate all $\mathrm{Ba^{2+}}$ in the solution?

Solution

Solutions to Example 13.8.1

Steps for Problem Solving	Example 15.8.1
Identify the "given" information and what the problem is asking you to "find."	Given: 275 mL $BaCl_2$ 0.250 M $BaCl_2$ or $\frac{0.250\ mol BaCl_2}{1\ L\ BaCl_2\ solution}$ 0.500 M Na_2SO_4 or $\frac{0.500\ mol Na_2SO_4}{1\ L\ Na_2SO_4\ solution}$ Find: Volume Na_2SO_4 solution.
Set up and balance the chemical equation.	$Na_2SO_4(aq) + BaCl_2(aq) \longrightarrow BaSO_4(s) + 2NaCl(aq)$ An insoluble product is formed after the reaction.
List other known quantities.	1 mol of Na_2SO_4 to 1 mol $BaCl_2$ 1000 mL = 1 L
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$275\ \cancel{mL\ BaCl_2\ solution} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times \frac{0.250\ \cancel{mol\ BaCl_2}}{1\ \cancel{L\ BaCl_2\ solution}} \times \frac{1\ \cancel{mol\ Na_2SO_4}}{1\ \cancel{mol\ BaCl_2}} \times \frac{1\ L\ Na_2SO_4\ solution}{0.500\ \cancel{mol Na_2SO_4}}$ = 0.1375 L sodium sulfate
Think about your result.	The lesser amount (almost half) of sodium sulfate is to be expected as it is more concentrated than barium chloride. Also, the units are correct.

? EXERCISE 15.8.1

What volume of 0.250 M lithium hydroxide will completely react with 0.500 L of 0.250 M of sulfuric acid solution?

Answer

0.250 L LiOH solution

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15.9: 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 $1\ \text{atm}$ 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 $0.20\ \text{m}$ solution of table salt and a $0.20\ \text{m}$ 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 $0.20\ \text{m}$ solution of table salt and a $0.20\ \text{m}$ solution of hydrochloric acid would have the same effect on the freezing point.

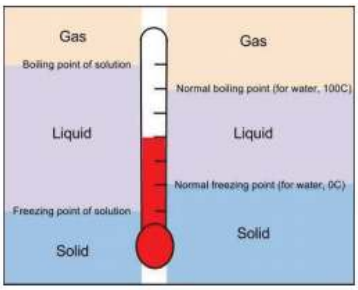


Figure 15.9.1: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

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 NaCl however, adding 10 formulas of solute to the solution will produce 20 ions (solute particles) in the solution. Therefore, adding enough NaCl solute to a solvent to produce a $0.20\ \mathrm{m}$ solution will have twice the effect of adding enough sugar to a solvent to produce a $0.20\ \mathrm{m}$ 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, NaCl, will dissociate into two ions so for NaCl, $i = 2$; for lithium nitrate, $\mathrm{LiNO_3}$, $i = 2$; and for calcium chloride, $\mathrm{CaCl_2}$, $i = 3$. 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 (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 15.9.1

Rank the following solutions in water in order of *increasing* (lowest to highest) freezing point:

- $0.1\ \mathrm{m\ NaCl}$
- $0.1\ \mathrm{m\ C_6H_{12}O_6}$
- $0.1\ \mathrm{m\ CaI_2}$

Solution

To compare freezing points, we need to know the total concentration of all particles when the solute has been dissolved.

- $0.1\ \mathrm{m\ NaCl}$: This compound is ionic (metal with nonmetal), and will dissolve into 2 parts. The total final concentration is: $(0.1\ \mathrm{m})\,(2) = 0.2\ \mathrm{m}$
- $0.1\ \mathrm{m\ C_6H_{12}O_6}$: This compound is covalent (nonmetal with nonmetal), and will stay as 1 part. The total final concentration is: $(0.1\ \mathrm{m})\,(1) = 0.1\ \mathrm{m}$
- $0.1\ \mathrm{m\ CaI_2}$: This compound is ionic (metal with nonmetal), and will dissolve into 3 parts. The total final concentration is: $(0.1\ \mathrm{m})\,(3) = 0.3\ \mathrm{m}$

Remember, the greater the concentration of particles, the lower the freezing point will be. $0.1\ \mathrm{m\ CaI_2}$ will have the lowest freezing point, followed by $0.1\ \mathrm{m\ NaCl}$, and the highest of the three solutions will be $0.1\ \mathrm{m\ C_6H_{12}O_6}$, 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°C while the boiling point of a 2% saltwater solution is about 102°C. Therefore, the boiling point elevation would be 2°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:

$$\Delta T_b = k_b \cdot \text{m} \cdot i \tag{15.9.1}$$

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°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:

$$\Delta T_f = k_f \cdot \text{m} \cdot i \tag{15.9.2}$$

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°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 15.9.2: 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°C? The freezing point constant, k_f, for water is 1.86°C/m.

Solution

Use the equation for freezing point depression of solution (Equation 15.9.2):

$$\Delta T_f = k_f \cdot \text{m} \cdot i$$

Substituting in the appropriate values we get:

$$2.64^\circ\text{C} = (1.86^\circ\text{C/m})\,(\text{m})\,(1)$$

Solve for m by dividing both sides by 1.86°C/m.

$$\text{m} = 1.42$$

Example 15.9.3: 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 15.9.1):

$$\Delta T_b = k_b \cdot \mathrm{m} \cdot i$$

We need to be able to substitute each variable into this equation.

- $k_b = 0.52^{\circ}\mathrm{C/m}$
- m: We must solve for this using stoichiometry. Given: 10.0 g NaCland 100.0 g H_2OFind: mol NaCl/kg H_2O. Ratios: molar mass of NaCl, 1000 g = 1 kg

$$\frac{10.0 \text{ g NaCl}}{100.0 \text{ g } H_2O} \cdot \frac{1 \text{ mol NaCl}}{58.45 \text{ g NaCl}} \cdot \frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O} = 1.71 \text{ m}$$

- For NaCl, $i = 2$

Substitute these values into the equation $\Delta T_b = k_b \cdot \mathrm{m} \cdot i$. We get:

$$\Delta T_b = \left(0.52 \frac{^{\circ}\mathrm{C}}{\text{m}}\right)(1.71 \text{ m})(2) = 1.78^{\circ}\mathrm{C}$$

Water normally boils at $100^{\circ}\mathrm{C}$, but our calculation shows that the boiling point increased by $1.78^{\circ}\mathrm{C}$. Our new boiling point is $101.78^{\circ}\mathrm{C}$.

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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15.10: Osmosis

Learning Objectives

- Explain the following laws within the Ideal Gas Law

Before we introduce the final colligative property, we need to present a new concept. A **semipermeable membrane** is a thin membrane that will pass certain small molecules, but not others. A thin sheet of cellophane, for example, acts as a semipermeable membrane. Consider the system in Figure 15.10.1

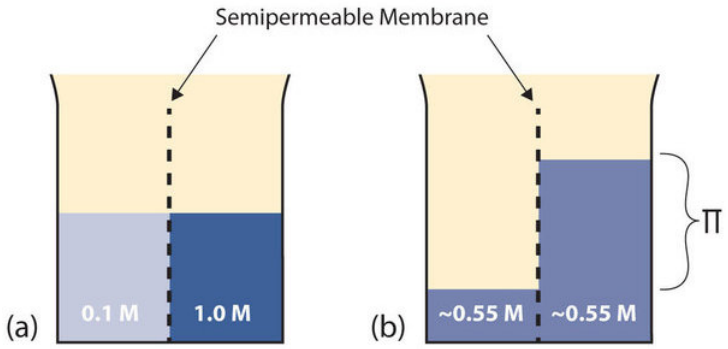


Figure 15.10.1: Osmosis. (a) Two solutions of differing concentrations are placed on either side of a semipermeable membrane. (b) When osmosis occurs, solvent molecules selectively pass through the membrane from the dilute solution to the concentrated solution, diluting it until the two concentrations are the same. The pressure exerted by the different height of the solution on the right is called the osmotic pressure. (CC BY-SA-NC 3.0; anonymous)

a. A semipermeable membrane separates two solutions having the different concentrations marked. Curiously, this situation is not stable; there is a tendency for water molecules to move from the dilute side (on the left) to the concentrated side (on the right) until the concentrations are equalized, as in Figure 15.10.1*b*
b. This tendency is called **osmosis**. In osmosis, the solute remains in its original side of the system; only solvent molecules move through the semipermeable membrane. In the end, the two sides of the system will have different volumes. Because a column of liquid exerts a pressure, there is a pressure difference (Π) on the two sides of the system that is proportional to the height of the taller column. This pressure difference is called the **osmotic pressure**, which is a colligative property.

The osmotic pressure of a solution is easy to calculate:

\[\Pi = MRT \nonumber \]

where Π is the osmotic pressure of a solution, *M* is the molarity of the solution, *R* is the ideal gas law constant, and *T* is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in Chapter 6.

Example 15.10.5: Osmotic Pressure

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?

Solution

First we need to convert our temperature to kelvins:

$$T = 25 + 273 = 298 \text{ K}$$

Now we can substitute into the equation for osmotic pressure, recalling the value for *R*:

$$\Pi = (0.333M)\left(0.08205\frac{L.atm}{mol.K}\right)(298K)$$

The units may not make sense until we realize that molarity is defined as moles per liter:

$$\Pi = \left(0.333\frac{mol}{L}\right)\left(0.08205\frac{L.atm}{mol.K}\right)(298K)$$

Now we see that the moles, liters, and kelvins cancel, leaving atmospheres, which is a unit of pressure. Solving,

$$\Pi = 8.14\, atm$$

This is a substantial pressure! It is the equivalent of a column of water 84 m tall.

? Exercise 15.10.5

What is the osmotic pressure of a 0.0522 M solution of $C_{12}H_{22}O_{11}$ at 55°C?

Answer

1.40 atm

Osmotic pressure is important in biological systems because cell walls are semipermeable membranes. In particular, when a person is receiving intravenous (IV) fluids, the osmotic pressure of the fluid needs to be approximately the same as blood serum to avoid any negative consequences. Figure 15.10.3shows three red blood cells:

- A healthy red blood cell.
- A red blood cell that has been exposed to a lower concentration than normal blood serum (a *hypotonic* solution); the cell has plumped up as solvent moves into the cell to dilute the solutes inside.
- A red blood cell exposed to a higher concentration than normal blood serum (*hypertonic*); water leaves the red blood cell, so it collapses onto itself. Only when the solutions inside and outside the cell are the same (*isotonic*) will the red blood cell be able to do its job.

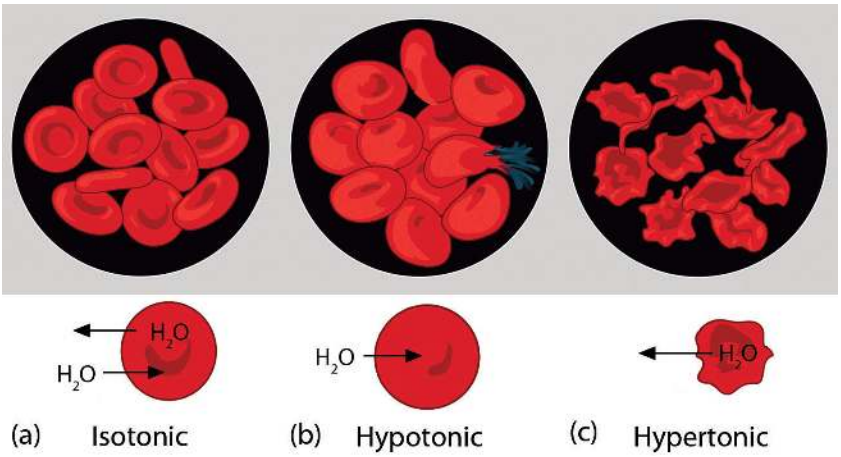


Figure 15.10.3: Osmotic Pressure and Red Blood Cells. (a) This is what a normal red blood cell looks like. (b) When a red blood cell is exposed to a hypotonic solution, solvent goes through the cell membrane and dilutes the inside of the cell. (c) When a red blood cell is exposed to a hypertonic solution, solvent goes from the cell to the surrounding solution, diluting the hypertonic solution and collapsing the cell. Neither of these last two cases is desirable, so IV solutions must be isotonic with blood serum to not cause deleterious effects. (Public Domain; Mariana Ruiz Villareal)

Osmotic pressure is also the reason you should not drink seawater if you're stranded on a lifeboat in the ocean; seawater has a higher osmotic pressure than most of the fluids in your body. You *can* drink the water, but ingesting it will pull water out of your cells as osmosis works to dilute the seawater. Ironically, your cells will die of thirst, and you will also die. (It is okay to drink the water if you are stranded on a body of freshwater, at least from an osmotic pressure perspective.) Osmotic pressure is also thought to be important—in addition to capillary action—in getting water to the tops of tall trees.

Summary

- Osmotic pressure is caused by concentration differences between solutions separated by a semipermeable membrane, and is an important biological consideration.

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CHAPTER OVERVIEW

16: Acids and Bases

Acids and bases are common substances found in many every day items, from fruit juices and soft drinks to soap. In this chapter, we will examine the properties of acids and bases, and learn about the chemical nature of these important compounds. We will cover pH, and how to calculate the pH of a solution.

16.1: Acids- Properties and Examples
16.2: Bases- Properties and Examples
16.3: Molecular Definitions of Acids and Bases
16.4: Reactions of Acids and Bases
16.5: Acid–Base Titration
16.6: Strong and Weak Acids and Bases
16.7: Water - Acid and Base in One
16.8: The pH and pOH Scales - Ways to Express Acidity and Basicity
16.9: Buffers- Solutions that Resist pH Change

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16.1: Acids- Properties and Examples

Learning Objectives

- Examine properties of acids.

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.

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 indicates. 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:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{16.1.1}$$

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.

It should not be hard for you to name several common acids (but you might find that listing bases is a little more difficult). Below is a partial list of some common acids, along with some chemical formulas:

Table 16.1.1: Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid is HCl	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 "fizz" 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.

What exactly makes an acid an acid, and what makes a base act as a base? Take a look at the formulas given in the above table and take a guess.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. A colorless, highly pungent solution of hydrogen chloride (HCl) in water. Hydrochloric acid is usually prepared by treating HCl with water.

$$\mathrm{HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)}$$

Hydrochloric acid can therefore be used to prepare chloride salts. Hydrochloric acid is a strong acid, since it is completely dissociated in water. Hydrochloric acid is the preferred acid in titration for determining the amount of bases.

Sulfuric Acid

Sulfuric acid is a highly corrosive strong mineral acid with the molecular formula $\mathrm{H_2SO_4}$. Sulfuric acid is a diprotic acid and has a wide range of applications including use in domestic acidic drain cleaners,[as an electrolyte in lead-acid batteries, and in various cleaning agents. It is also a central substance in the chemical industry.



Figure 16.1.1: 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 ($\mathrm{H_2O}$) 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 16.1.2).

$$\mathrm{M + H_2SO_4 \rightarrow M(SO_4) + H_2} \tag{16.1.2}$$

Nitric Acid

Nitric acid ($\mathrm{HNO_3}$) 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. Nitric acid can be made by reacting nitrogen dioxide ($\mathrm{NO_2(g)}$) with water.

$$\mathrm{3\,NO_2(g) + H_2O(l) \rightarrow 2\,HNO_3(ag) + NO(g)}$$

Nitric acid reacts with most metals, but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals (e.g., nitric acid with magnesium, manganese or zinc will liberate $\mathrm{H_2}$ gas):

$$\mathrm{Mg + 2\,HNO_3 \rightarrow Mg(NO_3)_2 + H_2}$$

$$\mathrm{Mn + 2\,HNO_3 \rightarrow Mn(NO_3)_2 + H_2}$$

$$\mathrm{Zn + 2\,HNO_3 \rightarrow Zn(NO_3)_2 + H_2}$$

Nitric acid is a corrosive acid and a powerful oxidizing agent. The major hazard it poses is chemical burn, as it carries out acid hydrolysis with proteins (amide) and fats (ester) which consequently decomposes living tissue (Figure 16.1.2). Concentrated nitric acid stains human skin yellow due to its reaction with the keratin



Figure 16.1.2: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Carbonic Acid

Carbonic acid is a chemical compound with the chemical formula $\mathrm{H_2CO_3}$ and is also a name sometimes given to solutions of carbon dioxide in water (carbonated water), because such solutions contain small amounts of $\mathrm{H_2CO_3(aq)}$. Carbonic acid, which is a weak acid, forms two kinds of salts: the carbonates and the bicarbonates. In geology, carbonic acid causes limestone to dissolve, producing calcium bicarbonate—which leads to many limestone features such as stalactites and stalagmites. Carbonic acid is a polyprotic acid, specifically it is diprotic, meaning that it has two protons which may dissociate from the parent molecule.

When carbon dioxide dissolves in water, it exists in chemical equilibrium (discussed in Chapter 15), producing carbonic acid:

$$\mathrm{CO_2 + H_2O \rightleftharpoons H_2CO_3}$$

The reaction can be pushed to favor the reactants to generate $\mathrm{CO_2(g)}$ from solution, which is key to the bubbles observed in carbonated beverages (Figure 16.1.3).



Figure 16.1.3: A glass of sparkling water. (CC BY-SA 3.0; Nevit Dilmen).

Formic Acid

Formic acid ($\mathrm{HCO_2H}$) is the simplest carboxylic acid and is an important intermediate in chemical synthesis and occurs naturally, most notably in some ants. The word "formic" comes from the Latin word for ant, formica, referring to its early isolation by the distillation of ant bodies. Formic acid occurs widely in nature as its conjugate base formate.

Citric Acid

Citric acid ($\mathrm{C_6H_8O_7}$) is a weak organic tricarboxylic acid that occurs naturally in citrus fruits. The citrate ion is an intermediate in the TCA cycle (Krebs cycle), a central metabolic pathway for animals, plants and bacteria. Because it is one of the stronger edible acids, the dominant use of citric acid is used as a flavoring and preservative in food and beverages, especially soft drinks.



Figure 16.1.4: Lemons, oranges, limes, and other citrus fruits possess high concentrations of citric acid (CC BY-SA 2.5; André Karwath).

Acetylsalicylic Acid

Acetylsalicylic acid (also known as aspirin) is a medication used to treat pain, fever, and inflammation. Aspirin, in the form of leaves from the willow tree, has been used for its health effects for at least 2,400 years.

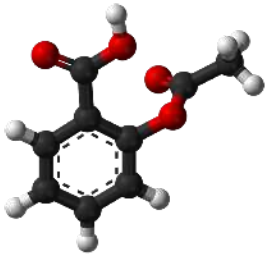


Figure 16.1.5: Ball-and-stick model of the aspirin molecule. (Public Domain; Ben Mills).

Aspirin is a white, crystalline, weakly acidic substance.

Summary

A brief summary of key aspects of several acids commonly encountered by students was given. Acids are a distinct class of compounds because of the properties of their aqueous solutions.

Contributions & Attributions

-
- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

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16.2: Bases- Properties and Examples

Learning Objectives

- Examine properties of bases.

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.

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.



Figure 16.2.1: 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.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. **Antacids**, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate. Various common bases and corresponding uses are given in Table 16.2.2

Table 16.2.1: Common Bases and Corresponding 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.

Some Common Bases	Uses
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula NaOH. It is a white solid ionic compound consisting of sodium cations $\mathrm{Na^+}$ and hydroxide anions $\mathrm{OH^-}$.

Dissolution of solid sodium hydroxide in water is a highly exothermic reaction:

$$\mathrm{NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)}$$

The resulting solution is usually colorless and odorless and feels slippery when it comes in contact with skin.



Figure 16.2.1: Sample of sodium hydroxide as pellets in a watch glass. (Public Domain; Walkerma.)

Potassium Hydroxide

Potassium hydroxide is an inorganic compound with the formula KOH, and is commonly called caustic potash. Along with sodium hydroxide (NaOH), this colorless solid is a prototypical strong base. It has many industrial and niche applications, most of which exploit its corrosive nature and its reactivity toward acids. Its dissolution in water is strongly exothermic.

$$\mathrm{KOH(s) \rightarrow K^+(aq) + OH^-(aq)}$$

Concentrated aqueous solutions are sometimes called *potassium lyes*.

Magnesium Hydroxide

Magnesium hydroxide is the inorganic compound with the chemical formula $\mathrm{Mg(OH)_2}$. Magnesium hydroxide is a common component of antacids, such as milk of magnesia, as well as laxatives.



Figure 16.2.1: Bottle of Antacid tablets. (CC BY 2.,5; Midnightcomm).

It is a white solid with low solubility in water. Combining a solution of many magnesium salts with basic water induces precipitation of solid $\mathrm{Mg(OH)_2}$. However, a weak concentration of dissociated ions can be found in solution:

$$\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)}$$

Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathrm{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime. Calcium hydroxide is used in many applications, including food preparation. Limewater is the common name for a saturated solution of calcium hydroxide.

Calcium hydroxide is relatively insoluble in water, but is large enough that its solutions are basic according to the following reaction:

$$\mathrm{Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)}$$

Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula $\mathrm{NH_3}$ and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

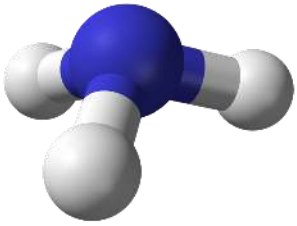


Figure 16.2.1: Ball-and-stick model of the ammonia molecule. (Public Domain; Ben Mills).

In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from $\mathrm{H_2O}$ to yield ammonium and hydroxide ions:

$$\mathrm{NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$$

Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

- A brief summary of properties of bases was given.
- The properties of bases mostly contrast those of acids.
- Bases have many, varied uses.

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16.3: Molecular Definitions of Acids and Bases

Learning Objectives

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

There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces H^+ in solution and a base produces OH^-. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; the Lewis theory is discussed elsewhere.

The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that **increases the concentration of H^+ ions** that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

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

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. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

The Brønsted-Lowry Theory of Acids and Bases

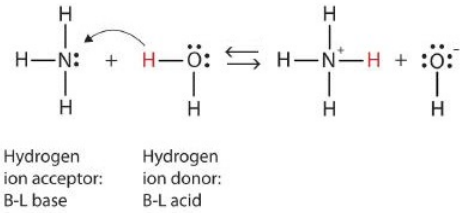
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, **a Brønsted-Lowry acid** is a **proton donor (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:

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{16.3.1}$$

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:

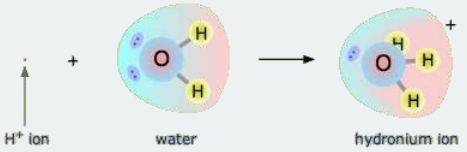


Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

The Hydronium Ion

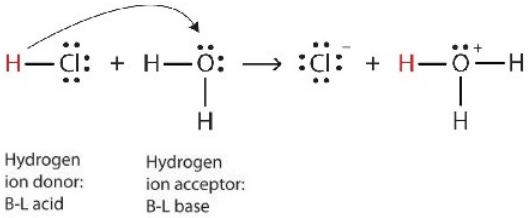
A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+ to represent the hydronium ion.



With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{16.3.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; 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 Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

- All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Example 16.3.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise 16.3.1

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

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

Answer

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

Exercise 16.3.2

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 HCl, H_3PO_4, NH_4^+ and $CH_3NH_3^+$ because they are Bronsted-Lowry acids. They all give away protons. In the case of HPO_4^{2-}, consider the following equation:

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

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:

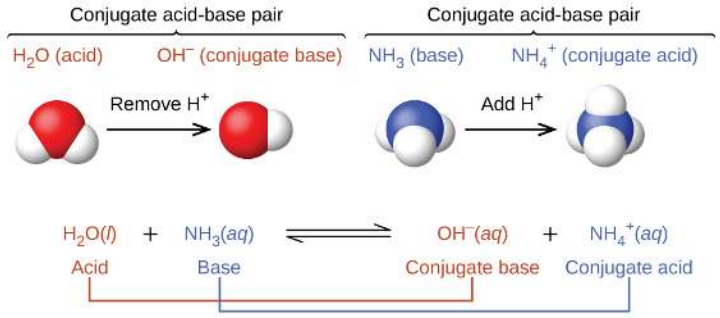
$$HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)$$

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, $\mathrm{OH^-}$, and the conjugate acid of ammonia, $\mathrm{NH_4^+}$:



This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

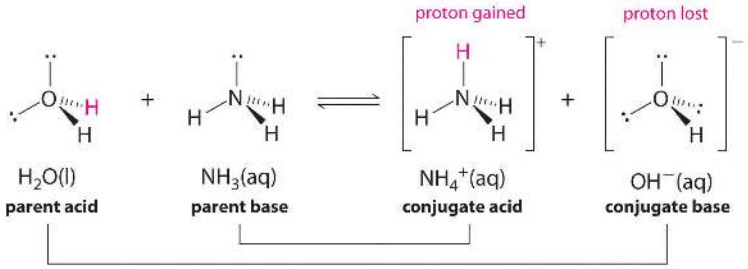


Figure 16.3.1. The pairing of parent acids and bases with conjugate acids and bases.

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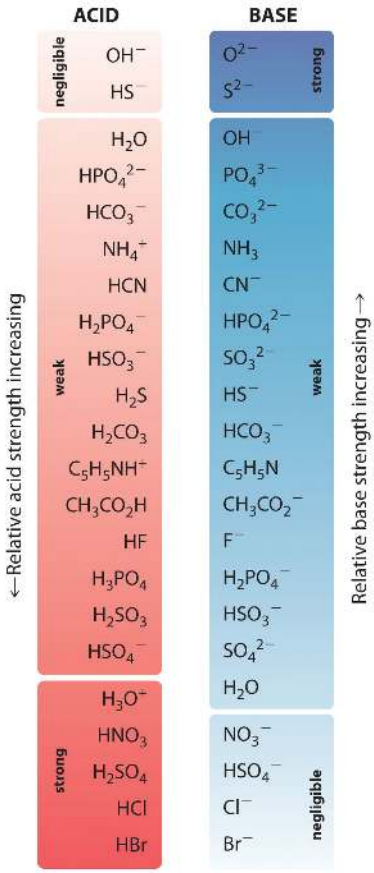


Figure 16.3.1: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Example 16.3.2

Identify the conjugate acid-base pairs in this equilibrium.

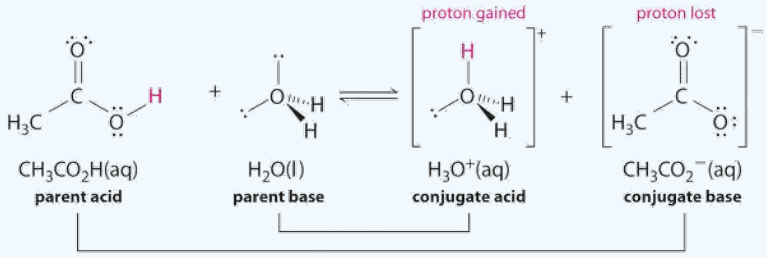
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 16.3.3

Identify the conjugate acid-base pairs in this equilibrium.

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

Solution

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

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

Exercise 16.3.3

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)

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16.4: Reactions of Acids and Bases

Learning Objectives

- Write acid-base neutralization reactions.
- Write reactions of acids with metals.
- Write reactions of bases with metals.

Neutralization Reactions

The reaction that happens when an acid, such as HCl, is mixed with a base, such as NaOH:

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

When an acid and a base are combined, water and a salt are the products. Salts are ionic compounds containing a positive ion other than $\mathrm{H^+}$ and a negative ion other than the hydroxide ion, $\mathrm{OH^-}$. 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:

$$\mathrm{H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)}$$

After removing the spectator ions, we get the net ionic equation:

$$\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)}$$

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. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic.



Video: Equimolar (~0.01 M) and equivolume solutions of HCl and NaOH are combined to make salt water. https://youtu.be/TS-I9KrUjB0

Example 16.4.1: 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

Solutions to Example 14.5.1

Steps	Reaction

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 16.4.1

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

Answer

$$Ba(OH)_2(s) + 2\,CH_3CO_2H(aq) \rightarrow Ba(CH_3CO_2)_2(aq) + 2\,H_2O(l)$$

Acids and Bases React with Metals

Acids react with most metals to form a salt and hydrogen gas. As discussed previously, metals that are more active than acids can undergo a **single displacement reaction**. For example, zinc metal reacts with hydrochloric acid, producing zinc chloride and hydrogen gas.

$$Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Bases also react with certain metals, like zinc or aluminum, to produce hydrogen gas. For example, sodium hydroxide reacts with zinc and water to form sodium zincate and hydrogen gas.

$$Zn(s) + 2\,NaOH(aq) + 2\,H_2O(l) \rightarrow Na_2Zn(OH)_4(aq) + H_2(g).$$

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16.5: Acid–Base Titration

Learning Objectives

- Understand the basics of acid-base titrations.
- Understand the use of indicators.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

During an acid-base titration, an acid with a known concentration (a **standard solution**) is slowly added to a base with an unknown concentration (or vice versa). A few drops of indicator solution are added to the base. The indicator will signal, by color change, when the base has been neutralized (when $[H^+] = [OH^-]$). At that point—called the **equivalence point,** or **end point**—the titration is stopped. By knowing the volumes of acid and base used, and the concentration of the standard solution, calculations allow us to determine the concentration of the other solution.

It is important to accurately measure volumes when doing titrations. The instrument you would use is called a burette (or buret).



Figure 16.5.1: Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\text{\# mol HCl} = (0.02566\ \text{L})(0.1078\ \text{M}) = 0.002766\ \text{mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ \cancel{mol\ HCl} \times \frac{1\ mol\ NaOH}{1\ \cancel{mol\ HCl}} = 0.002766\ mol\ NaOH$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ \cancel{mol\ HCl} \times \frac{40.00\ g\ NaOH}{1\ \cancel{mol\ HCl}} = 0.1106\ g\ NaOH$$

This type of calculation is performed as part of a titration.

Example 16.5.1: Equivalence Point

What mass of Ca(OH)2 is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO3? The balanced chemical equation is as follows:

$$2\ \text{HNO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Ca(NO}_3\text{)}_2 + 2\ \text{H}_2\text{O}$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

moles HNO_3 = (0.04402 L)(0.0885 M) = 0.00390 mol HNO_3

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ mol\ \cancel{HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ mol\ \cancel{HNO_3}} = 0.00195\ mol\ Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ mol\ \cancel{Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{mol\ \cancel{Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2$$

? Exercise 16.5.1

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2\,NaOH \rightarrow Na_2C_2O_4 + 2\,H_2O$$

Answer

0.182 g

? Exercise 16.5.2

If 25.00 mL of HCl solution with a concentration of 0.1234 M is neutralized by 23.45 mL of NaOH, what is the concentration of the base?

Answer

0.1316 M NaOH

? Exercise 16.5.3

A 20.0 mL solution of strontium hydroxide, $Sr(OH)_2$, is placed in a flask and a drop of indicator is added. The solution turns color after 25.0 mL of a standard 0.0500 M HCl solution is added. What was the original concentration of the $Sr(OH)_2$ solution?

Answer

$3.12 \times 10^{-2}\ M$ $Sr(OH)_2$

Indicator Selection for Titrations

The indicator used depends on the type of titration performed. The indicator of choice should change color when enough of one substance (acid or base) has been added to exactly use up the other substance. Only when a strong acid and a strong base are produced will the resulting solution be neutral. The three main types of acid-base titrations, and suggested indicators, are:

The three main types of acid-base titrations, suggested indicators, and explanations

Titration between . . .	Indicator	Explanation
strong acid and strong base	any	
strong acid and weak base	methyl orange	changes color in the acidic range (3.2 - 4.4)
weak acid and strong base	phenolphthalein	changes color in the basic range (8.2 - 10.6)

Summary

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all the analyte has reacted with the titrant.

Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

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16.6: 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.
- Determine if a salt produces an acidic or a basic solution.

Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in H_2O, it completely dissociates into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

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

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

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

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

As it turns out, there are very few strong acids, which are given in Table 16.6.1 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 16.6.1: 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 16.6.1); 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 16.6.1: 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 16.6.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 16.6.1, 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 16.6.1

Identify each acid or base as strong or weak.

a. RbOH
b. HNO_2

Answer a

strong base

Answer b

weak acid

Example 16.6.2: 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:

$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 16.6.1, this reaction proceeds 100% to products.

Exercise 16.6.2

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:

$$HN_3 \rightarrow H^+(aq) + N_3^-(aq)$$

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

Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

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16.7: Water - Acid and Base in One

Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of H_3O^+ and OH^- in aqueous solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:

$$\underbrace{NH_3}_{\text{base}} + \underbrace{H_2O}_{\text{acid}} \rightleftharpoons NH_4^+ + OH^-$$

where H_2O acts as an acid (in red).

$$\underbrace{HCl}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \longrightarrow H_3O^+ + Cl^-$$

where H_2O acts as an base (in blue).

It may not surprise you to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{16.7.1}$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**.

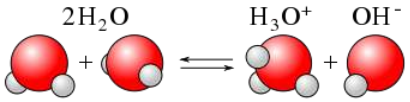


Figure 16.7.1: Autoionization of water, resulting in hydroxide and hydronium ions.

At this level, the concentration of both $H_3O^+(aq)$ and $OH^-(aq)$ in a sample of pure H_2O is about $1.0 \times 10^{-7}\ M$ (at room temperature). If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \tag{16.7.2}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H_3O^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of $H_3O^+(aq)$ (i.e., $[H_3O^+]$) is greater than $1.0 \times 10^{-7}\ M$.
- For bases the concentration of $OH^-(aq)$ (i.e., $[OH^-]$) is greater than $1.0 \times 10^{-7}\ M$.

However, the *product* of the two concentrations—$[H_3O^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_w:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{16.7.3}$$

This means that if you know $[H_3O^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}; or if you know $[OH^-]$), you can calculate $[H_3O^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

Warning: Temperature Matters

The degree of autoionization of water (Equation 16.7.1)—and hence the value of K_w—changes with temperature, so Equations 16.7.2 - 16.7.3 are accurate only at room temperature.

Example 16.7.1: Hydroxide Concentration

What is $[\mathrm{OH}^-]$) of an aqueous solution if $[\mathrm{H_3O}^+]$ is $1.0 \times 10^{-4} M$?

Solution

Solutions to Example 14.7.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $[\mathrm{H_3O}^+] = 1.0 \times 10^{-4}\ M$ Find: $[\mathrm{OH}^-]$ = ? M
List other known quantities.	none
Plan the problem.	Using the expression for K_w, (Equation 16.7.3), rearrange the equation algebraically to solve for $[\mathrm{OH}^-]$. $$[\mathrm{OH}^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$[\mathrm{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10}\ M$$ It is assumed that the concentration unit is molarity, so $[\mathrm{OH}^-]$ is 1.0×10^{-10} M.
Think about your result.	The concentration of the acid is high (> 1 x 10^{-7} M), so $[\mathrm{OH}^-]$ should be low.

Exercise 16.7.1

What is $[\mathrm{OH}^-]$ in a 0.00032 M solution of $\mathrm{H_2SO_4}$?

Hint

Assume **both** protons ionize from the molecule...although this is not the case.

Answer

$3.1 \times 10^{-11}\ M$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of $\mathrm{H_3O}^+$ or OH^- ions in the formula unit because $[\mathrm{H_3O}^+]$ or $[\mathrm{OH}^-]$) may not be the same as the concentration of the acid or base itself.

Example 16.7.2: Hydronium Concentration

What is $[\mathrm{H_3O}^+]$ in a 0.0044 M solution of $\mathrm{Ca(OH)_2}$?

Solution

Solutions to Example 14.7.2

Steps for Problem Solving	

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $[Ca(OH)_2] = 0.0044\,M$ Find: $[H_3O^+]$ = ? M
List other known quantities.	We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this: $$[OH^-]=2 \times 0 \cdot 0044\ M=0 \cdot 0088\ M\cdot$$
Plan the problem.	Use the expression for K_w (Equation 16.7.3) and rearrange the equation algebraically to solve for $[H_3O^+]$. $$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$[H_3O^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12}\,M$$ $[H_3O^+]$ has decreased significantly in this basic solution.
Think about your result.	The concentration of the base is high (> 1 x 10^{-7} M) so $[H_3O^+]$ should be low.

? Exercise 16.7.2

What is $[H_3O^+]$ of an aqueous solution if $[OH^-]$ is $1.0 \times 10^{-9}\ M$?

Answer

1.0×10^{-5} M

In any aqueous solution, the product of $[H_3O^+]$ and $[OH^-]$ equals 1.0×10^{-14} (at room temperature).

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16.8: The pH and pOH Scales - Ways to Express Acidity and Basicity

Learning Objectives

- Define pH and pOH.
- Determine the pH of acidic and basic solutions.
- Determine the hydronium ion concentration and pOH from pH.

As we have seen, $[H_3O^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of $[H_3O^+]$:

$$pH = -\log[H_3O^+] \tag{16.8.1}$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H_3O^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale. The pH scale is 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. Figure 16.8.1 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** $[H_3O^+]$, which will give a positive value for pH.

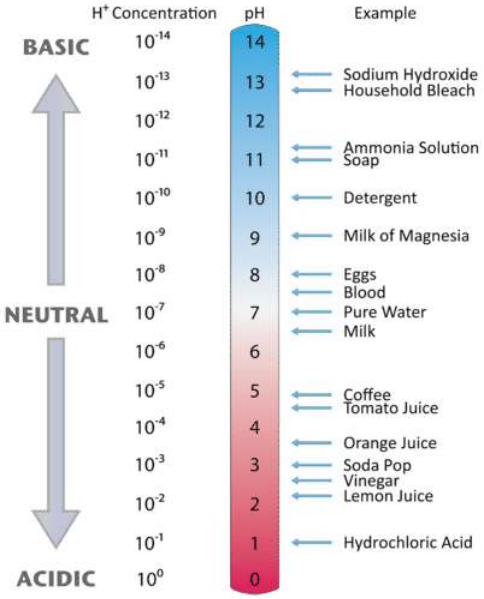


Figure 16.8.1: The pH values for several common materials.

Example 16.8.1

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 16.8.1

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

Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the pH of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

Logarithms

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x 10^{-5} (for $[H_3O^+]$ = 1.0 x 10^{-5} M) you should get an answer of "-5".

If you get a different answer, or an error, try pressing the LOG key before you enter the number.

Example 16.8.2: Converting Ph to Hydronium Concentration

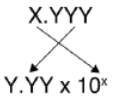
Find the pH, given the $[H_3O^+]$ of the following:

a. 1 ×10^{-3} M
b. 2.5 ×10^{-11} M
c. 4.7 ×10^{-9} M

Solution

Solutions to Example 14.9.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. $[H_3O^+]$ =1 × 10^{-3} M b. $[H_3O^+]$ =2.5 ×10^{-11} M c. $[H_3O^+]$ = 4.7 ×10^{-9} M Find: ? pH
Plan the problem.	Need to use the expression for pH (Equation 16.8.1). pH = - log $[H_3O^+]$

Steps for Problem Solving	
Calculate.	Now substitute the known quantity into the equation and solve. a. pH = - log [1 × 10^{-3}] = 3.0 (1 decimal places since 1 has 1 significant figure) b. pH = - log [2.5 ×10^{-11}] = 10.60 (2 decimal places since 2.5 has 2 significant figures) c. pH = - log [4.7 ×10^{-9}] = 8.30 (2 decimal places since 4.7 has 2 significant figures) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 16.8.2

Find the pH, given [H_3O^+] of the following:

a. 5.8 ×10^{-4} M
b. 1.0×10^{-7}

Answer a

3.22

Answer b

7.00

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation 16.8.1 for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[\mathrm{H_3O^+}] = \mathrm{antilog}(-pH)$$

or

$$[\mathrm{H_3O^+}] = 10^{-pH} \tag{16.8.2}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your*** calculator.

Calculator Skills

We have a solution with a pH = 8.3. What is [H_3O^+] ?

With some calculators you will do things in the following order:

1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key).
2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be 10^x.
3. You should get the answer **5.0 × 10^{-9}**.

Other calculators require you to enter keys in the order they appear in the equation.

1. Use the Shift or second function to key in the 10^x function.
2. Use the +/- key to type in a negative number, then type in 8.3.
3. You should get the answer **5.0×10^{-9}**.

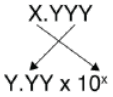
If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

Example 16.8.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

Solution

Solutions to Example 14.9.3

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem.	Need to use the expression for $[H_3O^+]$ (Equation 16.8.2). $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$
Calculate.	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.60) = 2.5 x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.60}$ = 2.5 x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 16.8.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5 x 10^{-8} M

The pOH scale

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$$\text{pOH} = -\log\left[\text{OH}^-\right]$$

The relation between the hydronium and hydroxide ion concentrations expressed as p-functions is easily derived from the K_w expression:

$$K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-] \tag{16.8.3}$$

$$-\log K_\text{w} = -\log([\text{H}_3\text{O}^+][\text{OH}^-]) = -\log[\text{H}_3\text{O}^+] + -\log[\text{OH}^-] \tag{16.8.4}$$

$$pK_w = pH + pOH \tag{16.8.5}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = pH + pOH \tag{16.8.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{16.8.7}$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{16.8.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Example 16.8.4:

Find the pOH of a solution with a pH of 4.42.

Solution

Solutions to Example 14.9.4

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH =4.42 Find: ? pOH
Plan the problem.	Need to use the expression pOH = 14 - pH
Calculate.	Now substitute the known quantity into the equation and solve. pOH=14−4.42=9.58
Think about your result.	The pH is that of an acidic solution, and the resulting pOH is the difference after subtracting from 14. The answer has two significant figures because the given pH has two decimal places.

Exercise 16.8.4

The pH of a solution is 8.22. What is the pOH?

Answer

5.78

The diagram below shows all of the interrelationships between [H3O+][H3O+], [OH−][OH−], pH, and pOH.

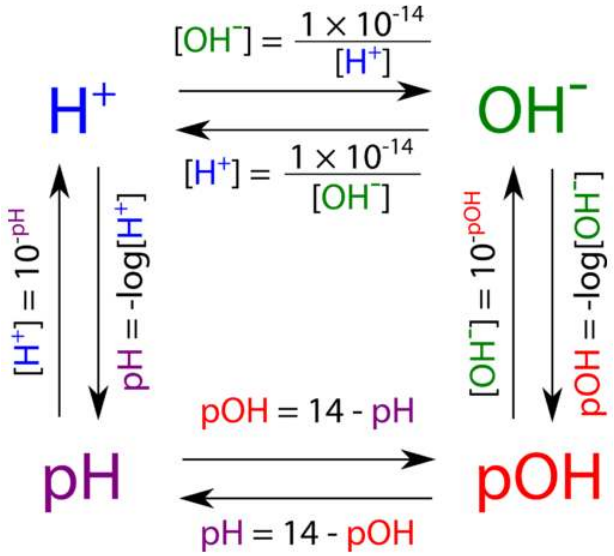


Figure 16.8.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
-
- Template:OpenStax

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16.9: Buffers- Solutions that Resist pH Change

Learning Objective

- Define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have marked chemical activity. 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 [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to life. 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 acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate ($NaC_2H_3O_2$, a salt derived from that acid). Another example of a buffer is a solution containing ammonia (NH_3, a weak base) and ammonium chloride (NH_4Cl, a salt derived from that base).

Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-(aq) \tag{16.9.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

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 hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) \tag{16.9.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 16.9.1 illustrates both actions of a buffer.

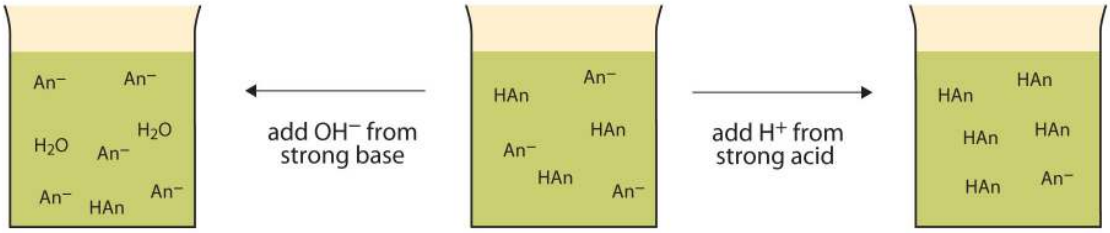


Figure 16.9.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) \tag{16.9.3}$$

while the **ammonium ion** ($NH_4^+(aq)$) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell) \tag{16.9.4}$$

Example 16.9.1: Making Buffer Solutions

Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl
d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is 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.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia with one of its hydrogen atoms substituted with a CH_3 (methyl) group. Because it is not on our list of strong bases, 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.
d. Ammonia (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 16.9.1

Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. 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.

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all 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 [H_2CO_3 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.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Contributions & Attributions

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CHAPTER OVERVIEW

17: Chemical Equilibrium

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.

17.1: The Rate of a Chemical Reaction
17.2: The Idea of Dynamic Chemical Equilibrium
17.3: The Equilibrium Constant - A Measure of How Far a Reaction Goes
17.4: Heterogeneous Equilibria- The Equilibrium Expression for Reactions Involving a Solid or a Liquid
17.5: Calculating and Using Equilibrium Constants
17.6: Disturbing a Reaction at Equilibrium- Le Châtelier's Principle
17.7: The Effect of a Concentration Change on Equilibrium
17.8: The Effect of a Volume Change on Equilibrium
17.9: The Effect of Temperature Changes on Equilibrium
17.10: The Solubility-Product Constant
17.11: The Path of a Reaction and the Effect of a Catalyst

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17.1: The Rate of a Chemical Reaction

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.

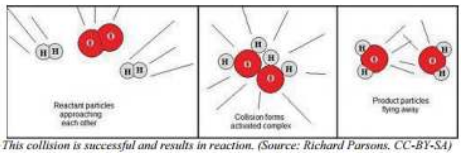
We know that a chemical system can be made up of atoms (H_2, N_2, K, etc.), ions (NO_3^-, Cl^-, Na^+, etc.), or molecules (H_2O, $C_{12}H_{22}O_{11}$, etc.). We also know that in a chemical system, these particles are moving around in random motion. The **collision theory** explains why reactions occur 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:

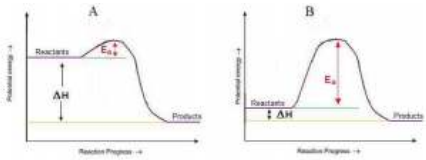
1. The particles must collide with each other.
2. The particles must collide with sufficient energy to break the old bonds.
3. The particles must have proper orientation.

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".

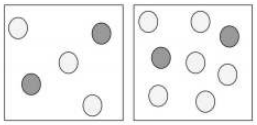
However, if that same carton of milk was at room temperature, the milk would react (in other words, "spoil") much more quickly. Most of the molecules would have sufficient energy to overcome the energy barrier at room temperature, and many more collisions would occur. This allows for the milk to spoil 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.

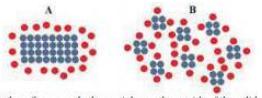


The reaction mixture on the left is less concentrated, so particles will not collide as often. The reaction will be slower. Because the reacting particles on the right image have a greater change of colliding, the reaction will go faster. CC – Tracy Poulsen

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 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.

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.

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.

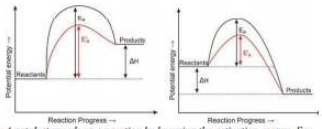
In the reaction of potassium chlorate breaking down to potassium chloride and oxygen, a catalyst is available to make this reaction occur much faster than it would occur by itself under room conditions. The reaction is:

$$2\mathrm{KClO_3}\,(s) \xrightarrow{\mathrm{MnO_2}(s)} 2\mathrm{KCl}\,(s) + 3\mathrm{O_2}\,(g)$$

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 $\mathrm{MnO_2}$ 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: $98.6^{\circ}\mathrm{F}$ or $37^{\circ}\mathrm{C}$. 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, $\mathrm{NO_2}$, a reddish-brown gas, reacts to form colorless dinitrogen tetroxide, $\mathrm{N_2O_4}$: $2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}$ But the reaction can also go the other way—dinitrogen tetroxide also readily breaks down to form nitrogen dioxide: $\mathrm{N_2O_4(g)} \rightarrow 2\,\mathrm{NO_2(g)}$ 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): $2\,\mathrm{NO_2(g)} \leftrightarrow \mathrm{N_2O_4(g)}$ Because the reaction continues in both directions at the same time, we never run out of either $\mathrm{NO_2}$ or $\mathrm{N_2O_4}$. $\mathrm{NO_2}$ is continually being used up to form $\mathrm{N_2O_4}$, but at the same time $\mathrm{N_2O_4}$ is forming more $\mathrm{NO_2}$

2.

When hydrogen gas is passed over heated iron oxide, iron and steam are produced:

(1)	$\mathrm{Fe_3O_4(s) + 4\,H_2(g) \rightarrow 3\,Fe(s) + 4}$
The reverse reaction can occur when steam is passed over red-hot iron:	
(2)	$\mathrm{3\,Fe(s) + 4\,H_2O(g) \rightarrow Fe_3O_4(s) +}$
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

$$\mathrm{3\,Fe(s) + 4\,H_2O(g) \leftrightarrow Fe_3O_4(s) + 4\,H_2(g)}$$

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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17.2: The Idea of Dynamic Chemical Equilibrium

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Learning Objectives

- Describe the three possibilities that exist when reactants come together.
- Describe what is occurring in a system at equilibrium.

Think for a minute about sitting down to a table to eat dinner. There are three possibilities that could happen when you eat dinner. You could (1) finish your entire dinner, (2) you could not want any of it and leave it all on your plate, or (3) you could eat some of it and leave some of it. Reactions have the same possibilities. Reactions do not always proceed all the way from start to finish. You may have reactions that (1) go to completion so that at the end, the reaction vessel contains all products and only products. Some reactions (2) may not start at all, so at the end the reaction vessel contains all reactants and only reactants. And some reactions (3) may start but not go to completion, that is, the reaction might start but not go completely to products. In this last case, the reaction vessel would contain some reactants and some products. In this section, we are going to take a closer look at the third type of reaction.

Reversible Reactions and Equilibrium

Consider the hypothetical reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}.$$

If we looked at this reaction using what we have learned, this reaction will keep going, forming C and D until A and B run out. This is what we call an "irreversible reaction" or a "reaction that goes to completion".

Some reactions, however, are **reversible**, meaning the reaction can go backwards in which products react to form reactants, so that: $\mathrm{A} + \mathrm{B} \leftarrow \mathrm{C} + \mathrm{D}$. The direction of the arrow shows that C and D are reacting to form A and B. What if the two reactions, the forward reaction and the reverse reaction, were occurring at the same time? What would this look like? If you could peer into the reaction, you would be able to find A, B, C, and D particles. A and B would react to form C and D at the same time that C and D are reacting to form A and B.

If the forward and reverse reactions are happening at the same rate, the reaction is said to be at **equilibrium** or **dynamic equilibrium**. At this point, the concentrations of A, B, C, and D are not changing (or, are constant) and we would see no difference in our reaction container, but reactions are still occurring in both directions. It is important to point out that having constant amounts of reactants and products does NOT mean that the concentration of the reactants is equal to the concentration of the products. It means they are not changing. These reactions appear to have stopped before one of the reactants has run out.

Chemists use a double-headed arrow, $\rightleftharpoons$, to show that a reaction is at equilibrium. We would write the example reaction as:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}.$$

The arrow indicates that both directions of the reaction are happening.

Another way to think about reversible and irreversible reactions is to compare them to two types of games of tag. Reversible reactions are in many ways like a traditional game of tag: the "it" person can become "not it" and somebody who is "not it" is tagged and becomes "it". In this way, it is a reversible change. It is also like a reaction at equilibrium, because overall no change is occurring. There is always a constant number of "it" people and "not it" people in the game. Also, having constant numbers of "it" and "not it" people in our game does not mean that the number of "it" people (reactants) is equal to the number of "not it" people (products). Furthermore, this is similar to equilibrium in that this game never truly ends (unless everybody gets tired of playing). The game could go on forever. We could write this as the following reversible reaction:

$$\text{"It"} \rightleftharpoons \text{"Not it"}$$

Irreversible reactions (those that only go in one direction from reactants to products and cannot reach a state of equilibrium) are more like a game of sharks and minnows. In sharks and minnows, almost everybody starts out as a minnow. Once tagged, they become a shark. However, the difference here is that once you are a shark you are always a shark; there is no way to go back to becoming a minnow. The game continues until everybody has been tagged and becomes a shark. This is similar to irreversible reactions in that the reactants turn into products, but can't change back. Furthermore, the reaction will proceed until the reactants have been used up and there are not any more left. We could write the reaction as:

$$\text{Minnow} \rightarrow \text{Shark}$$

Here's another example of a reversible reaction—dissolving salt in a beaker of water, described by the following reaction:

$$\text{NaCl(s)} \leftrightarrow \text{NaCl(aq)}$$

If you keep adding more and more solid salt, eventually you'll reach the point where no more salt dissolves, and the excess sits at the bottom of the beaker. At this point we have a saturated solution. Has the dissolving reaction stopped? It would appear so, but that's not the case (wouldn't that be too easy?).

What happens in our saturated solution, which has reached the point of **equilibrium**, is that both the forward

$$\text{NaCl(s)} \rightarrow \text{NaCl(aq)}$$

and reverse

$$\text{NaCl(aq)} \rightarrow \text{NaCl(s)}$$

reactions are still going on, but at the same ***rate***. This in effect cancels out any observable, or measurable, changes in our system. At the same rate that solid NaCl produces aqueous NaCl (dissolved salt), the dissolved salt is re-crystallizing to form more solid NaCl.

- **Equilibrium** is the state at which the rate of the forward reaction equals the rate of the reverse reaction.
- At the point of equilibrium, no more measurable or observable changes in the system can be noted.

It is important for you to understand that equilibrium means the ***rates*** of the forward and reverse reactions are equal; it does ***not*** mean that there are equal amounts of reactants and products present at equilibrium.

For example, the following reaction was allowed to come to the point of equilibrium, and concentrations of all reaction participants were measured at that time:

$$\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \leftrightarrow 2\,\text{HI(g)}$$

At equilibrium:	$[\text{H}_2] = 0.022\ \text{M}$ $[\text{I}_2] = 0.022\ \text{M}$ $[\text{HI}] = 0.156\ \text{M}$

For this particular reversible reaction, there is more HI at equilibrium (0.156 M) than there is of H_2 and I_2 (both at 0.022M). We say that the product side of the reaction is favored.

> *Equilibrium does not mean equal amounts at equilibrium!*

Here is an example to help you understand how equilibrium works: imagine yourself on a escalator that is going down. You start at the top (reactants) and end up at the bottom (products). But when you are partway down, you start walking up the escalator as it continues going down. If you match your rate of walking up to the same rate that the escalator is going down, you make no progress and appear to be at a standstill. To an observer it would look as if you and the escalator had come to a stop, when actually both upward and downward movements continue.

Equilibrium is **dynamic**—both forward and reverse reactions continue, even though the reaction appears to have stopped. And this equilibrium does not need to occur right in the middle of two floors—you could be near the bottom, near the top, or anywhere in between when you carry out your reverse process.

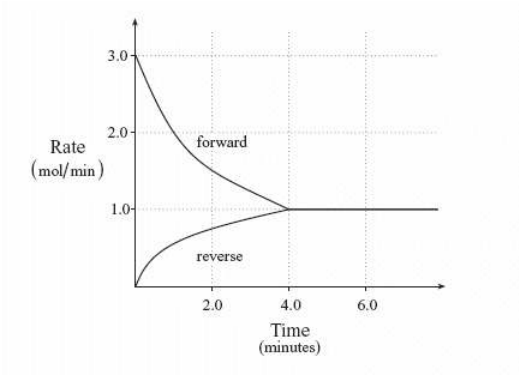
In order for a reversible reaction to reach the point of equilibrium, the reaction must be carried out in a closed system—no additional reactants can be added or products removed. If, in our last example, the product HI was removed as it formed, the

reaction would never reach the point of equilibrium; instead, H_2 and I_2 would continue to react to produce HI until one or both of the reactants was used up.

If reactants are constantly being added, and products removed as they form, the system would appear to be at equilibrium because to an outside observer it would appear that the reaction has stopped—but that would not be the case. This situation—with new material constantly being added as products are removed—is called a **steady state system**. A factory with an assembly line is a steady state system—new raw materials are constantly being added; finished products are removed. A campfire with wood being added to the fire is another steady state system. Be careful not to confuse steady state with equilibrium.

How do the rates of the forward and reverse reactions change as the reaction heads towards equilibrium (before it reaches equilibrium)?

If we start our above reaction with H_2 and I_2, and with no HI, the two gases will react at a certain rate. But remember that the rate of a reaction slows down over time, as the reactants get used up (and lower their concentrations). Eventually, however, the amount of the product HI increases, and it will begin producing H_2 and I_2. Thus the rate of the reverse reaction starts out slowly (there is no HI present), but will speed up as the concentration of HI increases. Eventually both rates will level off (not always to the same level as shown by this example, however):



Chemists have found that there is a mathematical relationship that exists between the concentration of the reactants and products, once equilibrium has been reached, that is independent of the initial concentration of the participants. For any general reaction,

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cD} + \mathrm{dD} \tag{17.2.1}$$

an equilibrium constant expression can be written as:

$$\mathrm{K_{eq}} = \frac{[\mathrm{C}]^{\mathrm{c}} \times [\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}} \times [\mathrm{B}]^{\mathrm{b}}} \tag{17.2.2}$$

This mathematical relationship exists for all equilibrium systems, and produces a constant ratio called the ***equilibrium constant, K_{eq}*** .

Law of Mass-Action

Equation 17.2.2 is sometimes called the Law of Mass-Action.

This relationship will be very important to us for the next few units, so it is important that you understand how to set this relationship up and what it tells us about an equilibrium system.

The products of the reaction (C and D) are placed in the numerator, and their concentrations are raised to the power of the coefficients from the balanced equation. The reactants (A and B) are placed in the denominator, with their concentrations raised to the power of *their* coefficients.

Example 17.2.1

For the reaction between hydrogen and iodine gas to produce hydrogen iodide:

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{HI(g)} \tag{17.2.3}$$

the equilibrium constant expression will be:

$$K_{eq} = \frac{[HI]^2}{[H_2] \times [I_2]} \tag{17.2.4}$$

Using the example we examined in our last section, equilibrium concentrations for each substance were measured at equilibrium and found to be:

At equilibrium:	$[H_2] = 0.022\ M$ $[I_2] = 0.022\ M$ $[HI] = 0.156\ M$

We substitute these values into our equilibrium expression and solve for K_{eq}:

$$K_{eq} = \frac{[HI]^2}{[H_2] \times [I_2]} = \frac{(0.156)^2}{(0.022)(0.022)} = 50.3$$

The value of K_{eq}, which has no units, is a constant for any particular reaction, and its value does not change unless the temperature of the system is changed. It does not depend on the initial concentrations used to reach the point of equilibrium.

For example, the following data were obtained for equilibrium concentrations of H_2, I_2 and HI, and the value of K_{eq} was calculated for each trial:

Trial	$[HI]$	$[H_2]$	$[I_2]$	K_{eq}
1	0.156	0.0220	0.0220	50.3
2	0.750	0.106	0.106	50.1
3	1.00	0.820	0.0242	50.4
4	1.00	0.0242	0.820	50.4
5	1.56	0.220	0.220	50.3

Aside from accounting for slight experimental variation between trials, the value for K_{eq} is the same despite differences in equilibrium concentrations for the individual participants.

There is one other important point to make at this time.

K_{eq} relates the concentrations of products to reactants at equilibrium.

For aqueous solutions, concentration is often measured as mol · L^{-1}. For gases, concentration is often measured as partial pressure.

The concentrations of both aqueous solutions and gases change during the progress of a reaction. For reactions involving a solid or a liquid, while the ***amounts*** of the solid or liquid will change during a reaction, their ***concentrations*** (much like their densities) will ***not*** change during the reaction. Instead, their values will remain constant. Because they are constant, their values **are not included in the equilibrium constant expression**.

Example 17.2.2

For example, consider the reaction showing the formation of solid calcium carbonate from solid calcium oxide and carbon dioxide gas:

$$\mathrm{CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s)}$$

The equilibrium constant for this reaction is (before modification):

$$\mathrm{K_{eq} = \frac{[CaCO_3]}{[CaO] \times [CO_2]}}$$

But we remove those participants whose state is either a solid or a liquid, which leaves us with the following equilibrium constant expression:

$$\mathrm{K_{eq} = \frac{1}{[CO_2]}}$$

Summary

- There are a few possible ways a reaction can go: it can go to completion ($\mathrm{reactants \rightarrow products}$), and it can occur but not go to completion. Instead, it will reach chemical equilibrium ($\mathrm{reactants \rightleftharpoons products}$).
- Chemical equilibrium occurs when the number of particles becoming products is equal to the number of particles becoming reactants.
- A dynamic equilibrium is a state where the rate of the forward reaction is equal to the rate of the reverse reaction.

Vocabulary

- **Equilibrium** - A state that occurs when the rate of the forward reaction is equal to the rate of the reverse reaction.

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17.3: The Equilibrium Constant - A Measure of How Far a Reaction Goes

Learning Objectives

- Write equilibrium constant expressions.
- Use equilibrium constant expressions to solve for unknown concentrations.
- Use known concentrations to solve for the equilibrium constants.
- Explain what the value of K means in terms of relative concentrations of reactants and products.

In the previous section, you learned about reactions that can reach a state of equilibrium, in which the concentration of reactants and products aren't changing. If these amounts are changing, we should be able to make a relationship between the amount of product and reactant when a reaction reaches equilibrium.

The Equilibrium Constant

Equilibrium reactions are those that do not go to completion, but are in a state where the reactants are reacting to yield products and the products are reacting to produce reactants. In a reaction at equilibrium, the equilibrium concentrations of all reactants and products can be measured. The **equilibrium constant (K)** is a mathematical relationship that shows how the concentrations of the products vary with the concentration of the reactants. Sometimes, subscripts are added to the equilibrium constant symbol K, such as K_{eq}, K_{c}, K_{p}, K_{a}, K_{b}, and K_{sp}. These are all equilibrium constants and are subscripted to indicate special types of equilibrium reactions.

There are some rules about writing equilibrium constant expressions that need to be learned:

1. Concentrations of products are multiplied on the top of the expression. Concentrations of reactants are multiplied together on the bottom.
2. Coefficients in the equation become exponents in the equilibrium constant expression.
3. Solids, liquids, and solvents are assigned a value of 1, so their concentrations do not affect the value of K.

Example 17.3.1

Write the equilibrium constant expression for:

$$\text{CO}\,(g) + 3\text{H}_2\,(g) \rightleftharpoons \text{CH}_4\,(g) + \text{H}_2\text{O}\,(g)$$

Solution

$$K = \frac{[\text{CH}_4]\,[\text{H}_2\text{O}]}{[\text{CO}]\,[\text{H}_2]^3}$$

*Note that the coefficients become exponents. Also, note that the concentrations of products in the numerator are *multiplied*. The same is true of the reactants in the denominator.

Example 17.3.2

Write the equilibrium constant expression for:

$$2\text{TiCl}_3\,(s) + 2\text{HCl}\,(g) \rightleftharpoons 2\text{TiCl}_4\,(s) + \text{H}_2\,(g)$$

Solution

$$K = \frac{[\text{H}_2]}{[\text{HCl}]^2}$$

*Note that the solids have a value of 1, and multiplying or dividing by 1 does not change the value of K.

Example 17.3.2

Write the equilibrium constant expression for:

$$\mathrm{P_4}\,(s) + 6\mathrm{Cl_2}\,(g) \rightleftharpoons 4\mathrm{PCl_3}\,(s)$$

Solution

$$K = \frac{1}{[\mathrm{Cl_2}]^6}$$

*Note that the only product is a solid, which is defined to have a value of 1. That leaves just 1 on top in the numerator.

Example 17.3.3

Write the equilibrium constant expression for:

$$\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

Solution

$$K = [\mathrm{H^+}]\,[\mathrm{OH^-}]$$

*Note that the water is the solvent, and thus has a value of 1. Dividing by 1 does not change the value of K.

Equilibrium Constant Expressions

The equilibrium constant value is the ratio of the concentrations of the products over the reactants. This means that we can use the value of K to predict whether there are more products or reactants at equilibrium for a given reaction. What can the value of K_{eq} tell us about a reaction?

- **If K_{eq} is very large**, the concentration of the products is much greater than the concentration of the reactants. The reaction essentially "goes to completion"; all, or most of, the reactants are used up to form the products.
- **If K_{eq} is very small**, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent—most of the reactants remain unchanged, and there are few products produced.
- **When K_{eq} is not very large or very small** (close to a value of 1) then roughly equal amounts of reactants and products are present at equilibrium.

Here are some examples to consider:

Reaction	Chemical Equations	Equilibrium Constant
the decomposition of ozone, $\mathrm{O_3}$	$2\,\mathrm{O_3(g)} \rightleftharpoons 3\,\mathrm{O_2(g)}$	$K_{eq} = 2.0 \times 10^{57}$
	K_{eq} is very large, indicating that mostly $\mathrm{O_2}$ is present in an equilibrium system, with very little $\mathrm{O_3}$.	
production of nitrogen monoxide	$\mathrm{N_2(g) + O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)}$	$K_{eq} = 1.0 \times 10^{-25}$
	Very little NO is produced by this reaction; $\mathrm{N_2}$ and $\mathrm{O_2}$ do not react readily to produce NO (this is lucky for us—otherwise we would have little oxygen to breath in our atmosphere!).	
reaction of carbon monoxide and water	$\mathrm{CO(g) + H_2O(g)} \rightleftharpoons \mathrm{CO_2(g) + H_2(g)}$	$K_{eq} = 5.09\,(\text{at } 700\text{ K})$
	The concentrations of the reactants are very close to the concentrations of the products at equilibrium.	

If the equilibrium constant is 1 or nearly 1, it indicates that the molarities of the reactants and products are about the same. If the equilibrium constant value is a large number, like 100, or a very large number, like 1×10^{15}, it indicates that the products (numerator) are a great deal larger than the reactants. This means that at equilibrium, the great majority of the material is in the form of products and it is said that the "products are strongly favored". If the equilibrium constant is small, like 0.10, or very small,

like 1×10^{-12}, it indicates that the reactants are much larger than the products and the reactants are strongly favored. With large K values, most of the material at equilibrium is in the form of products and with small K values, most of the material at equilibrium is in the form of the reactants.

The equilibrium constant expression is an equation that we can use to solve for K or for the concentration of a reactant or product.

Example 17.3.4

Determine the value of K for the reaction

$$\mathrm{SO_2}\,(g) + \mathrm{NO_2}\,(g) \rightleftharpoons \mathrm{SO_3}\,(g) + \mathrm{NO}\,(g)$$

when the equilibrium concentrations are: $[\mathrm{SO_2}] = 1.20\ \mathrm{M}$, $[\mathrm{NO_2}] = 0.60\ \mathrm{M}$, $[\mathrm{NO}] = 1.6\ \mathrm{M}$, and $[\mathrm{SO_3}] = 2.2\ \mathrm{M}$.

Solution

Step 1: Write the equilibrium constant expression:

$$K = \frac{[\mathrm{SO_3}]\,[\mathrm{NO}]}{[\mathrm{SO_2}]\,[\mathrm{NO_2}]}$$

Step 2: Substitute in given values and solve:

$$K = \frac{(2.2)\,(1.6)}{(1.20)\,(0.60)} = 4.9$$

Example 17.3.5

Consider the following reaction:

$$\mathrm{CO}\,(g) + \mathrm{H_2O}\,(g) \rightleftharpoons \mathrm{H_2}\,(g) + \mathrm{CO_2}\,(g)$$

with $K = 1.34$. If the $[\mathrm{H_2O}] = 0.100\ \mathrm{M}$, $[\mathrm{H_2}] = 0.100\ \mathrm{M}$, and $[\mathrm{CO_2}] = 0.100\ \mathrm{M}$ at equilibrium, what is the equilibrium concentration of CO?

Solution

Step 1: Write the equilibrium constant expression:

$$K = \frac{[\mathrm{H_2}]\,[\mathrm{CO_2}]}{[\mathrm{CO}]\,[\mathrm{H_2O}]}$$

Step 2: Substitute in given values and solve:

$$1.34 = \frac{(0.100)\,(0.100)}{[\mathrm{CO}]\,(0.100)}$$

Solving for $[\mathrm{CO}]$, we get: $[\mathrm{CO}] = 0.0746\ \mathrm{M}$

Summary

- The equilibrium constant expression is a mathematical relationship that shows how the concentrations of the products vary with the concentration of the reactants.
- If the value of K is greater than 1, the products in the reaction are favored. If the value of K is less than 1, the reactants in the reaction are favored. If K is equal to 1, neither reactants nor products are favored.

Vocabulary

- **Equilibrium constant** (K) - A mathematical ratio that shows the concentrations of the products divided by the concentrations of the reactants.

Contributions & Attributions

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17.4: Heterogeneous Equilibria- The Equilibrium Expression for Reactions Involving a Solid or a Liquid



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17.5: CALCULATING AND USING EQUILIBRIUM CONSTANTS

LEARNING OBJECTIVES

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)} \tag{17.5.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{\mathrm{CO}}^2}{a_{\mathrm{CO_2}} a_C} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}][1]} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}]} \tag{17.5.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{17.5.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and $\mathrm{CO_2}$, the system described in Equation 17.5.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure $17.5.1$, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

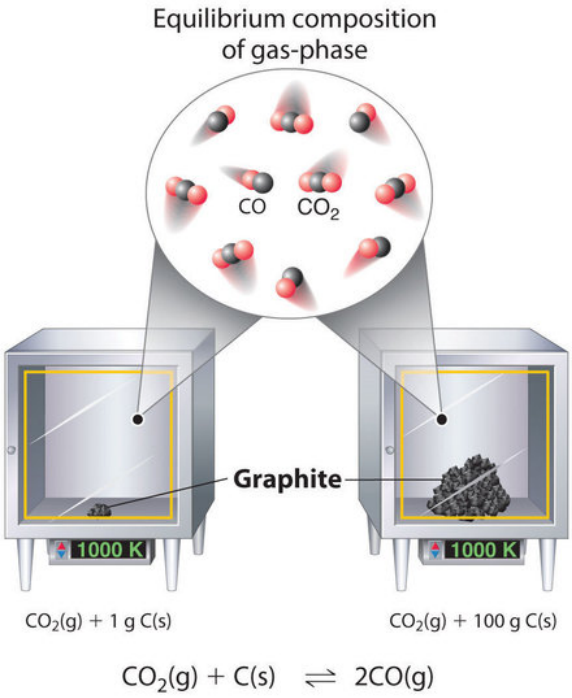


Figure 17.5.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

EXAMPLE 17.5.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)}$
b. $\mathrm{Fe_3O_4(s) + 4\,H_2(g) \rightleftharpoons 3\,Fe(s) + 4\,H_2O(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

EXERCISE 17.5.1

Write the expressions for K and K_p for the following reactions.

a. $\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$

b. $\underset{glucose}{\mathrm{C_6H_{12}O_6(s)}} + \mathrm{6\,O_2(g) \rightleftharpoons 6\,CO_2(g) + 6\,H_2O(g)}$

Answer a

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

Answer b

$K = \dfrac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \dfrac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

SUMMARY

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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17.6: DISTURBING A REACTION AT EQUILIBRIUM- LE CHÂTELIER'S PRINCIPLE

LEARNING OBJECTIVES

- State Le Chatelier's Principle.
- Describe the effect of concentration on an equilibrium system.
- Describe the effect of temperature as a stress on an equilibrium system.

When a reaction has reached equilibrium with a given set of conditions, if the conditions are not changed, the reaction will remain at equilibrium forever. The forward and reverse reactions continue at the same equal and opposite rates and the macroscopic properties remain constant.

It is possible, however, to disturb that equilibrium by changing conditions. For example, you could increase the concentration of one of the products, or decrease the concentration of one of the reactants, or change the temperature. When a change of this type is made within a reaction at equilibrium, the reaction is no longer in equilibrium. When you alter something in a reaction at equilibrium, chemists say that you put **stress** on the equilibrium. When this occurs, the reaction will no longer be in equilibrium and the reaction itself will begin changing the concentrations of reactants and products until the reaction comes to a new position of equilibrium. How a reaction will change when a stress is applied can be explained and predicted. That is the topic of this section.

LE CHATELIER'S PRINCIPLE

Think back to our escalator example, with you walking up a downward moving escalator. With the rate of the moving stairs and your walking evenly matched, you appear to be at a standstill. But what happens if the escalator begins moving just a little faster? If you want to maintain the same position you had, at some specific point between the bottom and the top of the stairs, you'll also need to make some adjustments. Chemical systems at equilibrium tend to make these adjustments as well.

In the late 1800's, a chemist by the name of Henry-Louis Le Chatelier was studying stresses that were applied to chemical equilibria. He formulated a principle from this research and, of course, the principle is called Le Chatelier's Principle. **Le Chatelier's Principle** states that when a stress is applied to a system at equilibrium, the equilibrium will shift in a direction to partially counteract the stress and once again reach equilibrium. Le Chatelier's principle is not an explanation of what happens on the molecular level to cause the equilibrium shift, it is simply a quick way to determine which way the reaction will run in response to a stress applied to the system at equilibrium.

LE CHATELIER'S PRINCIPLE

If a system at **equilibrium** is subjected to an external stress, the equilibrium will shift to **minimize** the effects of that stress.

Equilibrium is all about rates—the rate of the forward reaction is equal to the rate of the reverse reaction. External stresses are factors that will cause the rate of either the forward or reverse reaction to change, throwing the system out of balance. Le Chatelier's Principle allows us to predict how this will affect our system.

In our unit on Kinetics we examined factors that influenced reaction rates. Recall these factors:

1. concentration
2. pressure and volume
3. temperature
4. catalysts

We will see how changing these factors affects a system at equilibrium.

EFFECT OF CONCENTRATION CHANGES ON A SYSTEM AT EQUILIBRIUM

For instance, if a stress is applied by increasing the concentration of a reactant, the reaction will adjust in such a way that the reactants and products can get back to equilibrium. In the case of too much reactant, the reaction will use up some of the reactant to make more product. It is said in this scenario that the reaction "shifts to the products" or "shifts to the right". If the concentration of a product is increased, there is an opposite effect. The reaction will use up some of the product to make more reactant. The reaction "shifts to the reactants" or "shifts to the left".

What if some reactant or product is removed? If a stress is applied by lowering a reactant concentration, the reaction will try to replace some of the missing reactant. It uses up some of the product to make more reactant, and the reaction "shifts to the reactants". If a stress is applied by reducing the concentration of a product, the equilibrium position will shift toward the products.

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17.7: THE EFFECT OF A CONCENTRATION CHANGE ON EQUILIBRIUM

Consider the following system under equilibrium:

$$\underbrace{Fe^{3+}(aq)}_{\text{colorless}} + \underbrace{SCN^{-}(aq)}_{\text{colorless}} \rightleftharpoons \underbrace{FeSCN^{2+}(aq)}_{\text{red}}$$

If more Fe^{3+} is added to the reaction, what will happen?

According to Le Chatelier's Principle, the system will react to minimize the stress. Since Fe^{3+} is on the reactant side of this reaction, the rate of the forward reaction will increase in order to "use up" the additional reactant. This will cause the equilibrium to **shift to the right**, producing more $FeSCN^{2+}$. For this particular reaction, we will be able to see that this has happened, as the solution will become a darker red color.

There are a few different ways to state what happens here when more Fe^{3+} is added, all of which have the same meaning:

- equilibrium shifts to the right
- equilibrium shifts to the product side
- the forward reaction is favored

What changes does this cause in the concentrations of the reaction participants?

Changes within reaction participants

Fe^{3+}	Since this is what was added to cause the stress, the concentration of Fe^{3+} will increase. (A shorthand way to indicate this: $[Fe]^{3+} \uparrow$ (Reminder: the square brackets represent "concentration")
$SCN^{-}(aq)$	Equilibrium will shift to the right, which will use up the reactants. The concentration of $SCN^{-}(aq)$ will decrease $[SCN]^{-} \downarrow$ as the rate of the forward reaction increases.
$FeSCN^{2+}$	When the forward reaction rate increases, more products are produced, and the concentration of $FeSCN^{2+}$ will increase. $[FeSCN]^{2+} \uparrow$

How about the value of K_{eq}? Notice that the concentration of some reaction participants have increased, while others have decreased. Once equilibrium has re-established itself, the value of K_{eq} will be unchanged.

> *The value of K_{eq} does not change when changes in concentration cause a shift in equilibrium.*

What if more $FeSCN^{2+}$ is added?

Again, equilibrium will shift to use up the added substance. In this case, equilibrium will shift to favor the *reverse* reaction, since the reverse reaction will use up the additional $FeSCN^{2+}$.

- equilibrium shifts to the left
- equilibrium shifts to the reactant side
- the reverse reaction is favored

How do the concentrations of reaction participants change?

Change of concentrations of reaction participants when adding substance

Fe^{3+}	$[Fe]^{3+} \uparrow$ as the reverse reaction is favored
$SCN^{-}(aq)$	$[SCN]^{-} \uparrow$ as the reverse reaction is favored
$FeSCN^{2+}$	$[FeSCN]^{2+} \uparrow$ because this is the substance that was added

Concentration can also be changed by **removing** a substance from the reaction. This is often accomplished by adding another substance that reacts (in a side reaction) with something already in the reaction.

Let's remove SCN^- from the system (perhaps by adding some Pb^{2+} ions—the lead(II) ions will form a precipitate with SCN^-, removing them from the solution). What will happen now? Equilibrium will shift to **replace** SCN^-—the reverse reaction will be favored because that is the direction that produces more SCN^-.

- equilibrium shifts to the left
- equilibrium shifts to the reactant side
- the reverse reaction is favored

How do the concentrations of reaction participants change?

Change of concentrations of reaction participants when removing a substance	
Fe^{3+}	$[Fe]^{3+} \uparrow$ as the reverse reaction is favored
SCN^-	$[SCN]^- \uparrow$ as the reverse reaction is favored (but also ↓ because it was removed)
$FeSCN^{2+}$	$[FeSCN]^{2+} \uparrow$ because this is the substance that was added

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17.8: 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 17.8.1

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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17.9: THE EFFECT OF TEMPERATURE CHANGES ON EQUILIBRIUM

LEARNING OBJECTIVES

- Explain how temperature changes affect a system at equilibrium.

When temperature is the stress that affects a system at equilibrium, there are two important consequences:

- an increase in temperature will favor that reaction direction that ***absorbs*** heat (i.e. the endothermic reaction)
- the value of K_{eq} will change

Consider the following equilibrium system:

$$N_2O_4(g) \leftrightarrow 2\,NO_2(g)$$

$$\text{with } \Delta H^\circ = 58 \cdot 0 \text{ kJ}$$

We see by the sign of ΔH° that the forward reaction is endothermic. Heat is absorbed (required as a reactant) when the reaction proceeds as

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

By adding more heat, equilibrium will shift to use up the additional heat, thus favoring this forward direction.

Why will K_{eq} change, when it did not change when concentration, pressure, and volume were the applied stresses?

When temperature changes cause an equilibrium to shift, one entire side of the reaction equation is favored over the other side. Mathematically, this will alter the value of K_{eq} as follows:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

\ce{K_{eq}}

forward and reverse reactions

if the forward reaction is favored	more products are produced; fewer reactants	K_{eq} will increase
if the reverse reaction is favored	fewer products; more reactants	K_{eq} will decrease

So in our example given above, increasing the temperature will favor the forward direction. The value of K_{eq} will increase. **Removing heat (making the system colder) will favor the exothermic reaction**—the exothermic reaction ***releases heat*** to the surroundings, thus "replacing" the heat that has been removed.

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17.10: THE SOLUBILITY-PRODUCT CONSTANT

LEARNING OBJECTIVES

- Understand the basic concept of solution-solid equilibria.

We will now return to an important mathematical relationship that we first learned about in our unit on Equilibrium, the equilibrium constant expression. Recall that for any general reaction:

$$aA + bB \rightleftharpoons cD + dD$$

an equilibrium constant expression can be defined as:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Since saturated solutions are equilibrium systems, we can apply this mathematical relationship to solutions. We will refer to our equilibrium constant as K_{sp}, where "sp" stands for "solubility product"

For our silver sulfate saturated solution,

$$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + SO^{2-}_{4(aq)}$$

we can write a solubility product constant expression as

$$K_{sp} = \frac{[Ag^+_{(aq)}]^2[SO^{2-}_{4(aq)}]}{[Ag_2SO_{4(s)}]}$$

However, remember from our earlier introduction to the equilibrium constant expression that the concentrations of solids and liquids are ***NOT*** included in the expression because while their *amounts* will change during a reaction, their *concentrations* will remain constant. Therefore, we will write our solubility product constant expression for our saturated silver sulfate solution as:

$$K_{sp} = [Ag^+]^2[SO^{2-}_4]$$

Please note that it is **VERY IMPORTANT** to include the ion charges when writing this equation.

EXAMPLE 17.10.1

Write the expression for the solubility product constant, K_{sp}, for $Ca_3(PO_4)_2$.

Solution

Step 1: Begin by writing the balanced equation for the reaction. Remember that polyatomic ions remain together as a unit and do not break apart into separate elements.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Step 2: Write the expression for K_{sp}:

$$K_{sp} = [Ca^{2+}]^3[PO^{3-}_4]^2$$

Solubility Product Tables that give K_{sp} values for various ionic compounds are available. Because temperature affects solubility, values are given for specific temperatures (usually 25°C). Recall what we learned about K_{eq}:

- If K_{eq} is very large, the concentration of the products must be much greater than the concentration of the reactants. The reaction essentially "goes to completion", which means that all—or most of—the reactants are used up to form the products.
- If K_{eq} is very small, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent—most of the reactants remain unchanged, and there are few products produced.
- When K_{eq} is not very large or very small, then roughly equal amounts of reactants and products are present at equilibrium.

K_{sp}, which again is just a special case of K_{eq}, provides us with the same useful information:

A low value of K_{sp} indicates a substance that has a low solubility (it is generally insoluble); for ionic compounds this means that there will be few ions in solution.

- Iron(II) sulfide, FeS, is an example of a low K_{sp} : $K_{sp} = 4 \times 10^{-19}$. In a saturated solution of FeS there would be few Fe^{2+} or S^{2-} ions.

A large value of K_{sp} indicates a soluble substance; for ionic compounds it tells us that there will be many ions in solution.

- An example of a relatively large K_{sp} would be for lead(II) chloride, $PbCl_2$ which has a K_{sp} of 1.8×10^{-4}. A saturated solution of $PbCl_2$ would have a relatively high concentration of Pb^{2+} and Cl^- ions.

There are several types of problems we can solve:

EXAMPLE 17.10.1: CALCULATING K_{SP} OF A SATURATED SOLUTION

The concentration of a saturated solution of $BaSO_4$ is 3.90×10^{-5}M. Calculate K_{sp} for barium sulfate at 25°C.

Solution

Always begin problems involving K_{sp} by writing a balanced equation:

$$BaSO_{4\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Next, write the K_{sp} expression:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

The question provides us with the concentration of the solution, $BaSO_4$. We need to find the concentration of the individual ***ions*** for our equation.

Recall from Section 2.5: since 1 mole of $BaSO_4$ produces 1 mole of Ba^{2+} and also 1 mole of SO_4^{2-}, then...

- $[BaSO_4] = 3.90 \times 10^{-5}$M
- $[Ba^{2+}] = 3.90 \times 10^{-5}$M
- $[SO_4^{2-}] = 3.90 \times 10^{-5}$M

Substitute values into the K_{sp} expression and solve for the unknown:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$= (3.90 \times 10^{-5})(3.90 \times 10^{-5})$$

$$= 1.52 \times 10^{-9}$$

EXAMPLE 17.10.3: CALCULATING ION CONCENTRATIONS WHEN K_{SP} IS KNOWN

The K_{sp} for $MgCO_3$ at 25°C is 2.0×10^{-8}. What are the ion concentrations in a saturated solution at this temperature?

Solution

As always, begin with a balanced equation:

$$MgCO_{3(s)} \rightleftharpoons Mg^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Write the K_{sp} expression:

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

For this example, we are given the value for K_{sp} and need to find the ion concentrations.

We will let our unknown ion concentrations equal ***x***.

The balanced equation tells us that both Mg^{2+} and CO_3^{2-} will have the same concentration.

Substitute values into the equation and solve for the unknown:

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

$$x^2 = 2.0 \times 10^{-8}$$

$$x = \sqrt{(2.0 \times 10^{-8})}$$

find the square root of 2.0×10^{-8}:

$$= 1.4 \times 10^{-4}\text{M}$$

$$x = [Mg^{2+}]$$

$$= 1.4 \times 10^{-4}\text{M}$$

$$\text{AND } x = [CO_3^{2-}]$$

ANSWER

$= 1.4\times 10^{-4}M$

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17.11: 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:

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)}$$

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

18: Oxidation and Reduction

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.

18.1: Oxidation and Reduction- Some Definitions
18.2: Oxidation States- Electron Bookkeeping
18.3: Balancing Redox Equations
18.4: The Activity Series- Predicting Spontaneous Redox Reactions
18.5: Batteries- Using Chemistry to Generate Electricity
18.6: Electrolysis- Using Electricity to Do Chemistry
18.7: Corrosion- Undesirable Redox Reactions

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18.1: OXIDATION AND REDUCTION- SOME DEFINITIONS

"Redox" is short for "oxidation and reduction", two complimentary types of chemical reactions. The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion. **Reduction** originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.

These two terms have broader meanings now. In all oxidation-reduction reactions, an exchange of electrons occurs—one substance loses electrons while another gains them. That is the key to understanding redox reactions. We'll define these terms below.



Figure 18.1.1: *Reaction of copper wire in a silver nitrate solution.*

A simple demonstration of a redox reaction involves placing a solid piece of copper wire in a silver nitrate solution. Within minutes, the wire begins to look fuzzy or furry as small silver crystals begin to form on the wire. Meanwhile, the originally clear silver nitrate solution begins to take on a pale bluish tint. Furthermore, if the crystals are shaken off of the wire, we see that the wire partially disintegrated.

The overall equation for our demonstration describes the events:

$$\mathrm{Cu(s) + 2\,AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)}$$

Remember that when we have aqueous solutions of ionic compounds, the ions are really present as separate ions, not as bonded particles. So we can write an expanded equation:

$$\mathrm{Cu(s) + 2\,Ag^+(aq) + 2\,NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_3^-(aq) + 2\,Ag(s)}$$

Finally we remove spectator ions from the equation. Remember that spectator ions are ions that undergo no change during a reaction. Notice the nitrate ions, NO_3^-, they start as aqueous ions and end up exactly the same.

Removing the spectator ions gives us our **net ionic equation:**

$$\mathrm{Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)}$$

We can now see a bit more clearly what changes are occurring with this reaction.

OXIDATION OF COPPER METAL TO MAKE COPPER IONS

Copper began as a neutral atom with no charge, but changed into an ion with a charge of +2. An atom becomes a positive ion by losing electrons:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{18.1.1}$$

Notice that copper began as a solid, but is converted into aqueous ions—this is why the copper wire disintegrates. We say that copper was **oxidized** because it has lost electrons (i.e., electrons appear on the product side of the Equation 18.1.1).

REDUCTION OF SILVER IONS TO MAKE SILVER METAL

Silver was converted from an ion with a charge of +1, Ag+, to a neutral atom, Ag. The only way an ion can undergo this change is to gain an electron:

$$\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)} \tag{18.1.2}$$

Notice that solid silver is formed—this is what causes the fuzzy appearance to begin appearing on the wire—solid silver crystals. Silver has gained electrons, it has been reduced (i.e., electrons appear on the reactant side of Equation 18.1.2).

The electrons that silver gained had to come from somewhere—they came from copper. Conversely, a substance such as copper can only lose electrons if there is something else that will take them up, the silver ions. **One cannot occur without the other**. This exchange of electrons is what defines an **oxidation-reduction reaction**.

DEFINITION: OXIDATION

Oxidation is the **loss** of electrons.

DEFINITION: REDUCTION

Reduction is the **gain** of electrons.

You will be learning several new terms in this chapter and it is important that you learn them very quickly. You may find it useful to have some tricks to help you remember these terms, including the LEO/GER.

LEO THE LION SAYS GER

- LEO: Loss of Electrons is Oxidation.
- GER: Gain of Electrons is Reduction.



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18.2: Oxidation States- Electron Bookkeeping

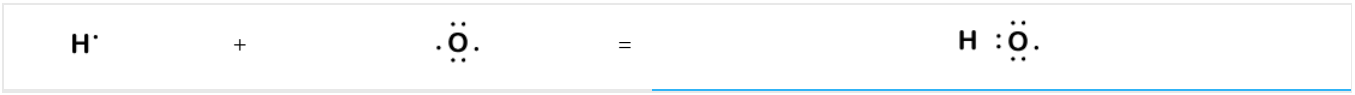
Redox reactions are all about electrons being transferred from one substance to another, so it is useful to have a system for keeping track of what gains and what loses electrons, and how many electrons are involved. The record-keeping system for redox reactions is called **Oxidation Numbers.** You may also remember something called **electronegativity** from earlier chemistry classes.

Electronegativity

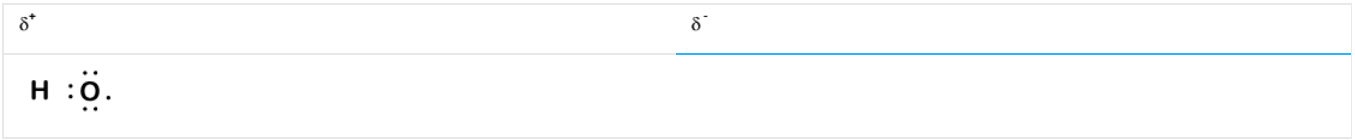
The ability of a bonded atom to attract shared electrons toward itself.

When two atoms of different elements are bonded together by a covalent bond (sharing electrons), the electrons are generally not shared equally between the two atoms due to differences in their electronegativities. Think of this as a tug-of-war for electrons. Sometimes both atoms pull with equal strength on shared electrons; other times there is clearly a stronger player that will pull the electrons closer to itself.

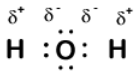
Consider the bond between a hydrogen atom (with one valence electron) and an oxygen atom (with its six valence electrons):



Because oxygen has a higher electronegativity than hydrogen, the shared electrons are closer to the oxygen atom than to the hydrogen atom. This is not the total transfer of electrons that would create an ion, but partial charges do form. The hydrogen end of the bond is partially positive (+1) because it has partially lost one electron, and the oxygen end of the H–O is partially negative (-1) because it has partially gained the one electron from hydrogen:



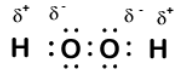
Our molecule is incomplete, however, because there is a lone electron around oxygen. Let's add one more hydrogen to complete our water molecule:



We see that each of the two hydrogens has "lost" one electron to oxygen. Oxygen has "gained" two electrons—one from each hydrogen. Again, these are not true ions, but it is useful to think of them in the same way.

Charges given to atoms in a molecule in this way are called **oxidation numbers**. We can use oxidation numbers to keep track of where electrons are in a molecule, and how they move during a reaction. In our water example, hydrogen is assigned an oxidation number of +1 because each individual hydrogen has "lost" one electron. Oxygen has an oxidation number of +2 because the single oxygen atom has "gained" a total of two electrons, one from each hydrogen.

Here is another molecule involving hydrogen and oxygen—hydrogen peroxide, H_2O_2:



In hydrogen peroxide, each hydrogen still has an oxidation number of +1 because each hydrogen "gives up" a single electron to oxygen. Oxygen, however, now has an oxidation number of -1 because each oxygen gains just one electron from its neighboring hydrogen. The electrons between the two identical oxygen atoms are shared equally, so there is no partial charge resulting from that bond.

Oxidation Number

A positive or negative number assigned to an atom in a molecule or ion that reflects a partial gain or loss of electrons.

Knowing the oxidation number of each individual element in a molecule will be a key step in our understanding of redox reactions. Fortunately it will not usually involve drawing electron dot diagrams. Instead, there are a series of rules that we can use to determine oxidation numbers. Here are the main rules:

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

2. The oxidation number of a monatomic ion (by itself or as part of an ionic compound) is equal to its charge.
Alkali metals—elements in the first column of the periodic table—will always have an oxidation number of +1; Alkaline earth metals (column 2) are almost always +2.

Ionic Compound	Ions	Charge	Oxidation Number
NaCl	Na^+	+1	+1
	Cl^-	-1	-1
Mg_3N_2	Mg^{+2}	+2	+2
	N^{-3}	-3	-3

3. The oxidation number of hydrogen is almost always +1 when it is in a compound.

Compound	Element	Oxidation Number
HCl	H	+1
	Cl	-1
H_2S	H	+1
	S	-2

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

4. The oxidation number of oxygen is almost always -2 when it is in a compound.
The exceptions:
- Peroxides, such as hydrogen peroxide. In peroxides, oxygen has an oxidation number of -1.
- When oxygen is combined with fluorine, its oxidation number is +2.

Compound	Element	Oxidation Number
MgO magnesium oxide	Mg	+2
	O	-2
Na_2O sodium oxide	Na	+1
	O	-2
Na_2O_2 sodium peroxide	Na	+1
	O	-1

5. The sum of the oxidation numbers in a compound is zero.
To determine the oxidation number of Mn in Mn_2O_7, we must work backwards:
- We know each oxygen is -2 (Rule 4).
- 7 oxygen gives a total of:

-2×7 atoms = -14 total

Since the sum of oxidation numbers must be zero, the total oxidation number of Mn must be +14 to cancel out oxygen's -14, but since there are 2 Mn atoms, each **individual atom** will have an oxidation number of +7:

$$\frac{+14 \text{ total}}{2 \text{ Mn atoms}} = +7$$

Compound	Element	Oxidation Number	Number of Atoms	Total
Mg_3N_2	Mg	+2	3	+6
	N	-3	2	-6
			SUM	0
Mn_2O_7	Mn	+7	2	+14
	O	-2	7	-14
			SUM	**0**
Cl_2O_3	Cl	+3	2	+6
	O	-2	3	-6
			SUM	**0**

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

6. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on that ion.
Again, work backwards to determine the oxidation number of any non-oxygen or non-hydrogen atom.
To determine the oxidation number of Cr in $Cr_2O_7^{2-}$:

- Oxygen will be -2 (Rule 4), for a total of:

$-2 \times 7 = -14$

- Since the sum of the oxidation numbers will be -2 (the charge on the entire ion), the total for all Cr must be +12 because:

+12 + (-14) = -2

- Since there are two Cr, each Cr will have an oxidation number of +6.

$= +7$

$$\frac{+12}{2} = +6$$

Compound	Element	Oxidation Number	Number of Atoms	Total
NO_3^-	N	+5	1	+5
	O	-2	3	-6
			SUM	-1
$Cr_2O_7^{2-}$	Cr	+6	2	+12
	O	-2	7	-14
			SUM	**-2**
SO_4^{2-}	S	+6	1	+6
	O	-2	4	-8
			SUM	**-2**

It is important to note that oxidation number always refers to ***each individual atom*** in the compound, not to the total for that element.

For example, in H_2O, the total positive "charge" for both hydrogen atoms will be +2 (which balances with the -2 from oxygen), but *each hydrogen* has an oxidation number of +1.

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18.3: 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		$\mathbf{Cu + 2\ AgNO_3 \rightarrow Cu(NO_3)_2 + 2\ Ag}$

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		$\mathbf{MnO_4^- + 5\ Fe^{2+} + 8\ H^+ \rightarrow Mn^{2+} + 5\ Fe^{3+} + 4H_2O}$

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		$\mathbf{2HNO_3 + Cu + 2H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O}$

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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18.4: The Activity Series- Predicting Spontaneous Redox Reactions

Learning Objectives

- Use the activity series to predict if a reaction will occur.

We see two metals below that can be exposed to water. The picture on the left is of sodium, which gives a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels.



Figure 18.4.1: On the left, sodium reacts with water. On the right, silver in the form of cups do not react with water.

The Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivities. The **activity series** is a list of elements in decreasing order of their reactivity. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The table below is an activity series of most common metals and of the halogens.

Table 18.4.1: Activity Series of Metals in Aqueous Solutions

Most Active (Easily Oxidized—Readily Lose Electrons)		
lithium	Li	These metals displace hydrogen from water $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_2 + H_{2\,(g)}$. These elements are very reactive and react readily to form compounds.
potassium	K	
barium	Ba	
calcium	Ca	
sodium	Na	
magnesium	Mg	These metals displace hydrogen from acids $Zn_{(s)} + HCl_{(aq)} \rightarrow ZnCl_2 + H_{2(g)}$
aluminum	Al	
zinc	Zn	
chromium	Cr	
iron	Fe	
cadmium	Cd	
nickel	Ni	
tin	Sn	
lead	Pb	
hydrogen	H	

Most Active (Easily Oxidized—Readily Lose Electrons)		
copper	Cu	These metals do not displace hydrogen from acids or water. These elements are more stable, and form compounds less readily than do those higher in the table.
silver	Ag	
mercury	Hg	
platinum	Pt	
gold	Au	
Least Active		

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron (III) nitrate and one of lead (II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$\mathrm{Ni}\,(s) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow \mathrm{Ni(NO_3)_2}\,(aq) + \mathrm{Pb}\,(s)$$

$$\mathrm{Ni}\,(s) + \mathrm{Fe(NO_3)_3}\,(aq) \rightarrow \mathrm{NR\ (no\ reaction)}$$

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and with acids, since that requires a lower degree of reactivity.

	Example 18.4.1	**Example 18.4.2**
Steps for Problem Solving	Use the activity series to predict if the reaction below will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation. $\mathrm{Al}\,(s) + \mathrm{Zn(NO_3)_2}\,(aq) \rightarrow$	Use the activity series to predict if the reaction below will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation. $\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow$
Plan the problem.	Compare the placements of aluminum (the element doing the replacing) and zinc (the element being replaced) on the activity series.	Compare the placements of silver (the element doing the replacing) and hydrogen (the element being replaced) on the activity series.
Solve.	Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a $+3$ charge in an ionic compound, so the formula for aluminum nitrate is $\mathrm{Al(NO_3)_3}$. The balanced equation is: $$\mathbf{2}\mathrm{Al}\,(s) + \mathbf{3}\mathrm{Zn(NO_3)_2}\,(aq) \rightarrow \mathbf{2}\mathrm{Al(NO_3)_3}\,(aq) + \mathbf{3}\mathrm{Zn}\,(s) \quad (18.4.1)$$	Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid. $$\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow \mathrm{NR} \quad (18.4.2)$$

? Exercise 18.4.1

Use the activity series to predict if the following reactions will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation.

a. Would it be possible to store a silver spoon in a zinc nitrate solution? That is, will the following reaction occur?

$$\ce{Ag_{(s)} + Zn(NO_3)_{2 (aq)} \rightarrow}$$

b. Would it be possible to store a silver nitrate solution in a copper container? That is, will the following reaction occur?

$$\ce{Cu_{(s)} + AgNO_{3 (aq)} \rightarrow}$$

Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the activity series.

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18.5: 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".

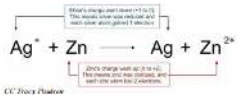
Originally, a substance was said to be oxidized when it reacted with oxygen. Today, the word "oxidized" is still used for those situations, but now we have a much broader second meaning for these words. Today, the broader sense of the word **oxidation** is defined as losing electrons. When a substance 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:

$$2\mathrm{Ag}^{+}(aq) + \mathrm{Cu}(s) \rightarrow 2\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq)$$

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:

$$2\mathrm{Ag}^{+}(aq) + 2\mathrm{e}^{-} \rightarrow 2\mathrm{Ag}(s)$$

$$\mathrm{Cu}(s) \rightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^{-}$$

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) $\mathrm{Zn} + \mathrm{HCl} \rightarrow \mathrm{H_2} + \mathrm{ZnCl_2}$

b) $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$

c) $\mathrm{NaBr} + \mathrm{I_2} \rightarrow \mathrm{NaI} + \mathrm{Br_2}$

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:

$$\mathrm{Zn}^{0} + \mathrm{H}^{+}\mathrm{Cl}^{-} \rightarrow \mathrm{H}_2^{0} + \mathrm{Zn}^{2+}\mathrm{Cl}_2^{-}$$

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:

$$\mathrm{Fe}^{0} + \mathrm{O}_2^{0} \rightarrow \mathrm{Fe}_2^{3+}\mathrm{O}_3^{2-}$$

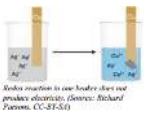
Fe is oxidized because it went from 0 to $+3$. O is reduced because it went from 0 to -2.

c) This reaction written with charges is:

$$\mathrm{Na}^{+}\mathrm{Br}^{-} + \mathrm{I}_2^{0} \rightarrow \mathrm{Na}^{+}\mathrm{I}^{-} + \mathrm{Br}_2^{0}$$

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


Redox reaction in one beaker does not produce electricity. (Source: Richard Parsons, CC-BY-SA)

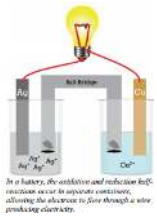
Batteries are devices that use chemical reactions to produce electrical energy. These reactions occur because the products contain less potential energy in their bonds than the reactants. The energy produced from excess potential energy not only allows the reaction to occur, but also often gives off 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:

$$2\mathrm{Ag}^{+}(aq) + \mathrm{Cu}(s) \rightarrow 2\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq)$$

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.



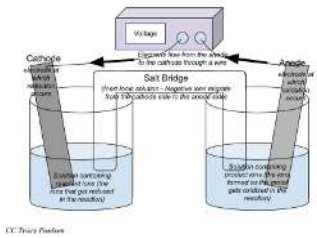
The reaction we just described is not set up in such a way as to produce electricity. It is true that electrons are being transferred, but to produce electricity, we need electrons flowing through a wire so that we can use the energy of these electrons. This reaction, $2Ag^{+}(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$, 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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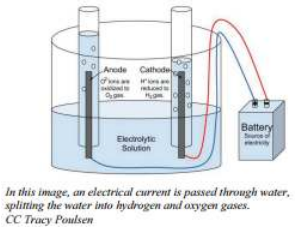
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18.6: Electrolysis- Using Electricity to Do Chemistry

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.

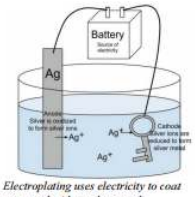


Figure 16.7.2: Silver plating.

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:

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

- Half-reaction at the anode:

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

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:

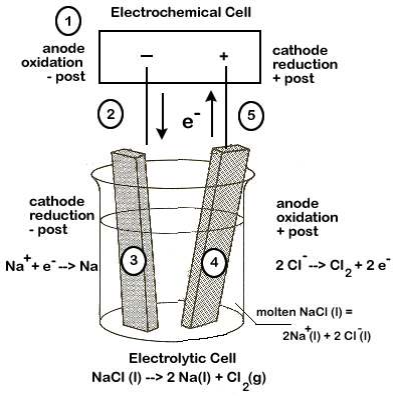
- The two half-reactions are not separated by a salt bridge.
- An electrochemical cell (or other source of electric current) will be required.

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:

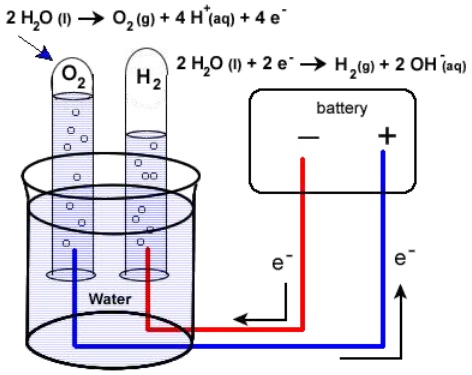
			E°
reduction	$2H_2O_{(l)} + 2e^- \rightarrow H_2 + 2\ OH^-$		-0.83 V
oxidation	$2H_2O_{(l)} \rightarrow O_2 + 4H^+ + 4e^-$		-1.23V
	(see note below for net equation)		
	net voltage required		**- 2.06V**

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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18.7: Corrosion- Undesirable Redox Reactions

Corrosion of metals is a serious economic problem. Corrosion occurs as a result of spontaneous electrochemical reaction as metal undergoes oxidation. For example, the rusting of iron begins with the oxidation of solid iron:

$$\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-}$$

The corresponding reduction reaction involves water:

$$\mathrm{H_2O(l) + \tfrac{1}{2}O_2(g) + 2\,e^- \rightarrow 2\,OH^-(aq)}$$

The flaky brown solid that we call rust forms when Fe^{2+} undergoes additional oxidation to form Fe^{3+}, then reacts with hydroxide ions to form iron (III) oxide, Fe_2O_3, and iron (III) hydroxide, $Fe(OH)_3$.

The rate of corrosion can be affected by several factors. Some examples:

- Metals corrode faster when in contact with another metal. The Statue of Liberty, for example, has a skin made of copper, but is supported by iron ribs. Since iron is oxidized more readily than copper, it acts as the anode. Earlier repairs to strengthen the statue used iron bolts, which exacerbated the problem. More recent repairs have replaced the iron ribs with stainless steel alloys. Stainless steel resists corrosion.
- Salt water speeds up the corrosion process, because the ions in salt water form a salt bridge between the anodic and cathodic sites. Salt may be great for icy roads, but it is tough on cars.

There are a number of ways to slow down corrosion, if not prevent it:

- Prevent oxygen and water from contacting the metal. This can be accomplished by paint, grease, plastic, or other methods of covering the metal.
- Cathodic protection: pieces of zinc or magnesium metal may be bolted to the surface of iron. Because they are more readily oxidized than Fe, Zn and Mg become oxidized over time, thus sparing and protecting the iron. Propeller shafts of speedboats are often protected this way. Anode rods in water heaters also work this way (they are often called **sacrificial anodes**). Galvanized nails—nails coated with the more reactive zinc—provide yet another example.
- Metal alloys: an alloy is a mixture of metals, or a mixture of a nonmetal with a metal. An alloy such as stainless steel (chromium is added to steel—a mixture of iron and other elements such as carbon—to make stainless steel) is highly resistant to corrosion, but can be prohibitively expensive.

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CHAPTER OVERVIEW

19: Radioactivity and Nuclear Chemistry

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.

19.1: The Discovery of Radioactivity
19.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay
19.3: Detecting Radioactivity
19.4: Natural Radioactivity and Half-Life
19.5: Radiocarbon Dating- Using Radioactivity to Measure the Age of Fossils and Other Artifacts
19.6: Radioactivity in Medicine
19.7: The Discovery of Fission and the Atomic Bomb
19.8: Nuclear Power- Using Fission to Generate Electricity
19.9: Nuclear Fusion- The Power of the Sun
19.10: The Effects of Radiation on Life

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19.1: 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 19.1.1: 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 $0.10\ \text{g}$ of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

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.

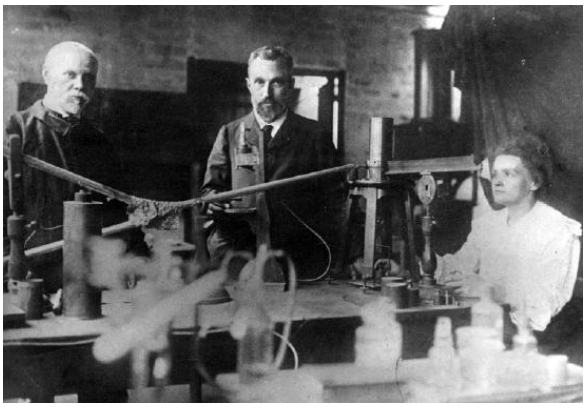


Figure 19.1.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

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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19.2: 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)

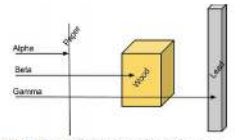
These particles were named using the first three letters of the Greek alphabet. Some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays, except much higher in energy and even more 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 19.2.1 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

$$^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th} \tag{19.2.1}$$

In this nuclear change, the uranium atom $\left({}^{238}_{92}\mathrm{U}\right)$ transmuted into an atom of thorium $\left({}^{234}_{90}\mathrm{Th}\right)$ and, in the process, gave off an alpha particle. Look at the symbol for the alpha particle: ${}^{4}_{2}\mathrm{He}$. 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.

$$^{230}_{90}\mathrm{Th} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{226}_{88}\mathrm{Ra} \tag{19.2.2}$$

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

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

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay:

$$ {}^{234}_{90}\text{Th} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{91}\text{Pa} \tag{19.2.3} $$

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 1×10^{3} 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 1×10^{18} 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

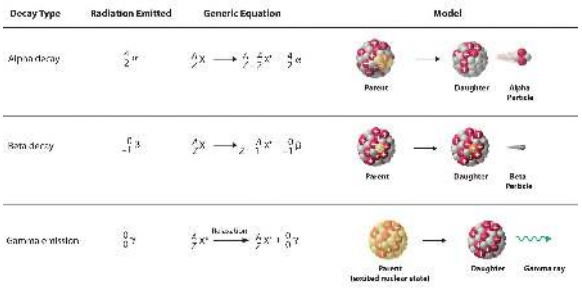


***Figure 17.3.2**: Three most common modes of nuclear decay.*

"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 19.2.1), 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 19.2.3):

- 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.

$$ {}^{234}_{91}\text{Pa} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{92}\text{U} \tag{19.2.4} $$

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 19.2.1, 19.2.3, 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 19.2.1

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 19.2.2

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.

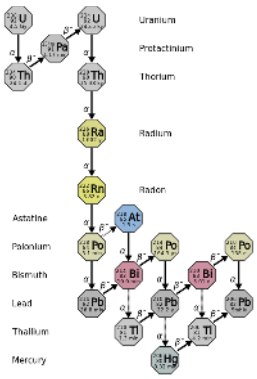


Figure 17.3.3: Uranium-238 decay chain. (CC-BY-3.0 Tosaka)

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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19.3: 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 19.3.1.

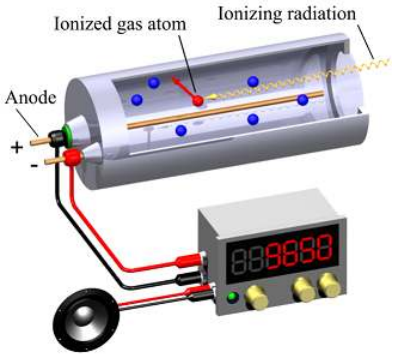


Figure 19.3.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

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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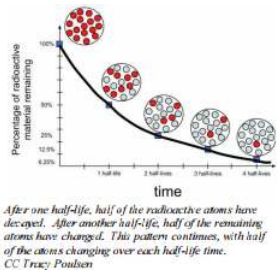
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19.4: Natural Radioactivity and Half-Life

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

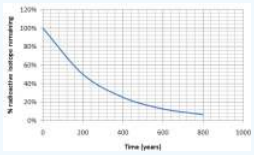
Element	Mass Number (A)	Half-life	Element	Mass Number (A)	Half Life
Uranium	238	4.5 Billion years	Californium	251	800 years
Neptunium	240	1 hour	Nobelium	254	3 seconds
Plutonium	243	5 hours	Carbon	14	5730 years
Americium	245	25 minutes	Carbon	16	740 milliseconds

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 19.4.3

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 19.4.2

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 19.4.3

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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19.5: 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.

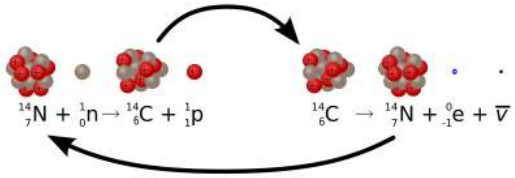


Figure 1: Diagram of the formation of carbon-14 (forward), the decay of carbon-14 (reverse). Carbon-14 is constantly generated in the atmosphere and cycled through the carbon and nitrogen cycles. Once an organism is de-coupled from these cycles (i.e., death), then the carbon-14 decays until there is 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.

$$^{14}\mathrm{C} \longrightarrow {}^{14}\mathrm{N} + \mathrm{e}^{-} + \mu_e \tag{19.5.1}$$

This follows first-order kinetics:

$$N_t = N_o e^{-kt} \tag{19.5.2}$$

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 19.5.2 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

$$k = \frac{\ln 2}{t_{1/2}} \tag{19.5.3}$$

so the rate constant is then

$$k = \frac{\ln 2}{5.73 \times 10^{3}} = 1.21 \times 10^{-4}\,\mathrm{year}^{-1} \tag{19.5.4}$$

and Equation 19.5.1 can be rewritten as

$$N_t = N_o e^{-\ln 2\ t/t_{1/2}} \tag{19.5.5}$$

or

$$t = \left(\frac{\ln \frac{N_o}{N_t}}{\ln 2} \right) t_{1/2} = 8267 \ln \frac{N_o}{N_t} = 19035 \log_{10} \frac{N_o}{N_t} \quad \text{(in years)} \tag{19.5.6}$$

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 19.5.6.

Note

Deriving Equation 19.5.6 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 19.5.6 must be corrected by using data from other sources.

Example 1: Dead Sea Scrolls

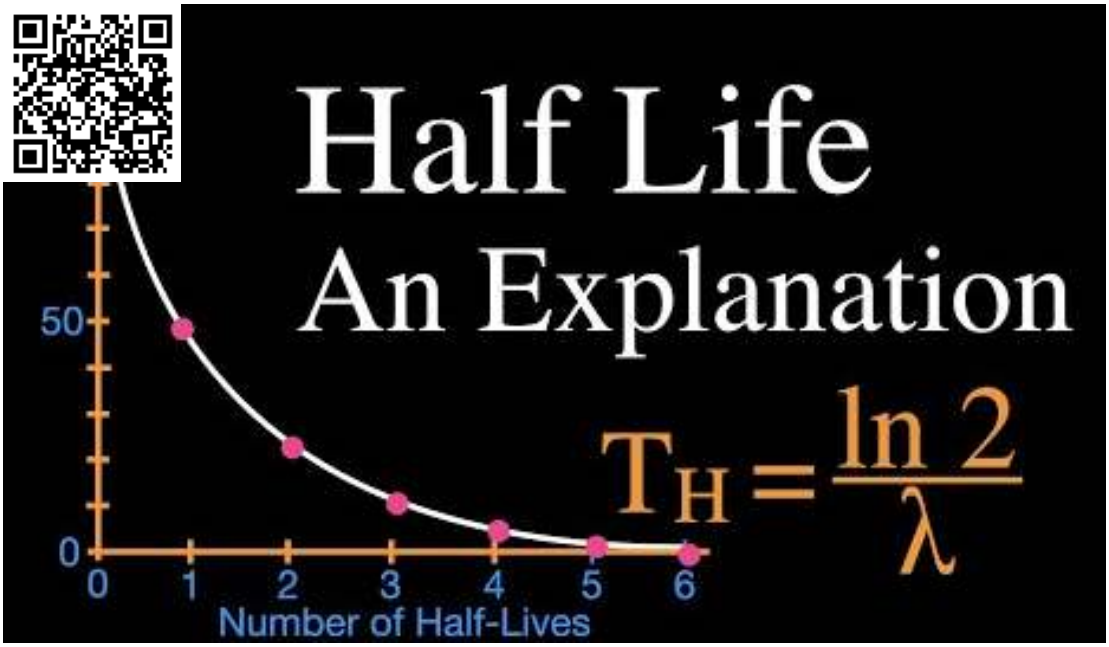
In 1947, samples of the Dead Sea Scrolls were analyzed by carbon dating. It was found that the carbon-14 present had an *activity* (rate of decay) of d/min.g (where d = disintegration). In contrast, living material exhibit an activity of 14 d/min.g. Thus, using Equation 19.5.2,

$$\ln \frac{14}{11} = (1.21 \times 10^{-4})t$$

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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1. Hua, Quan. "Radiocarbon: A Chronological Tool for the Recent Past." *Quaternary Geochronology* 4.5(2009):378-390. *Science Direct*. Web. 22 Nov. 2009.
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3. "Radio Carbon Dating." *BBC- Homepage*. 25 Oct. 2001. Web. 22 Nov. 2009. http://www.bbc.co.uk.
4. Willis, E.H., H. Tauber, and K. O. Munnich. "Variations in the Atmospheric Radiocarbon Concentration Over the Past 1300 Years." *American Journal of Science Radiocarbon Supplement* 2(1960) 1-4. Print.

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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19.6: 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 $(\mathrm{I}-131)$ 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 $(\mathrm{I}-131)$, 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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19.7: 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.

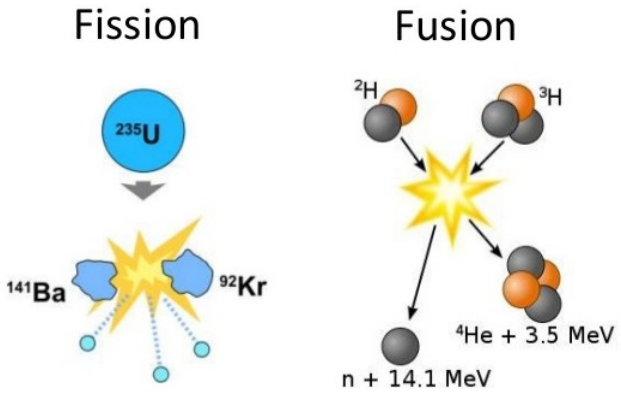


Figure 19.7.1: (left) Nuclear fission occurs when one large nucleus is split into two or more smaller nuclei. (right) Nuclear fusion happens when two small nuclei combine to make a larger nucleus.

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.

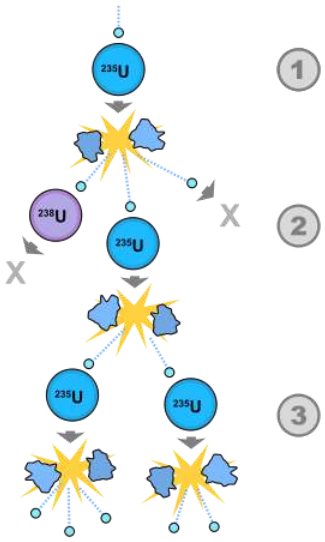


Figure 19.7.2: A possible nuclear fission chain reaction. 1. A uranium-235 atom absorbs a neutron, and fissions into two new atoms (fission fragments), releasing three new neutrons and a large amount of binding energy. 2. One of those neutrons is absorbed by an atom of uranium-238, and does not continue 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.

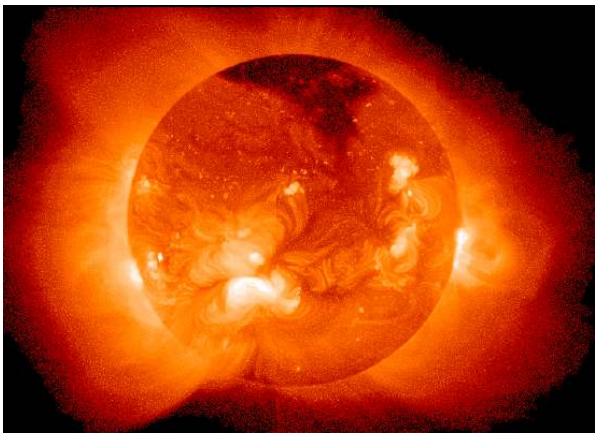


Figure 19.7.3: The energy that comes from the sun and other stars is produced by fusion. (Public Domain; NASA.)

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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19.8: 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.

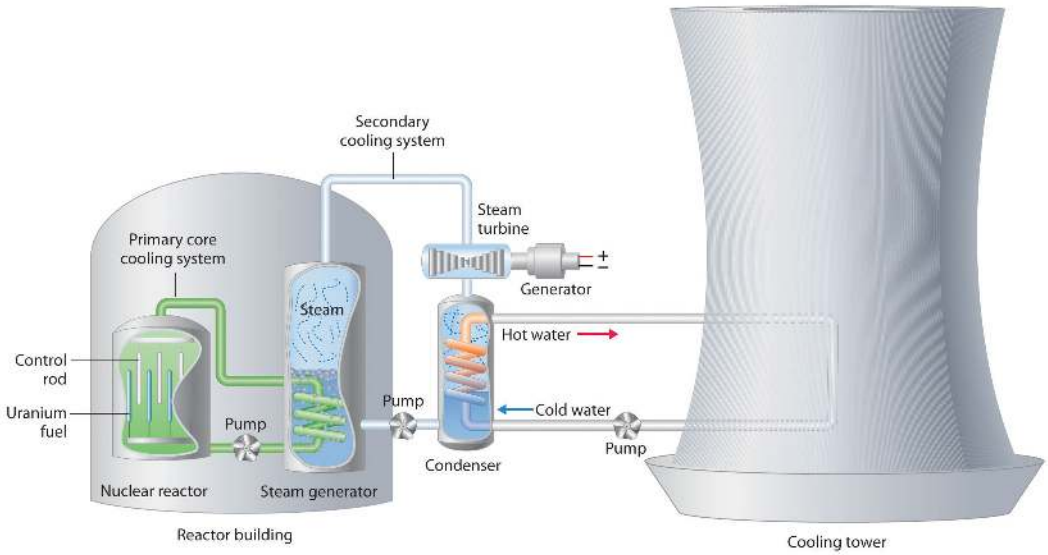


Figure 19.8.1: A Light-Water Nuclear Fission Reactor for the Production of Electric Power. The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic 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.

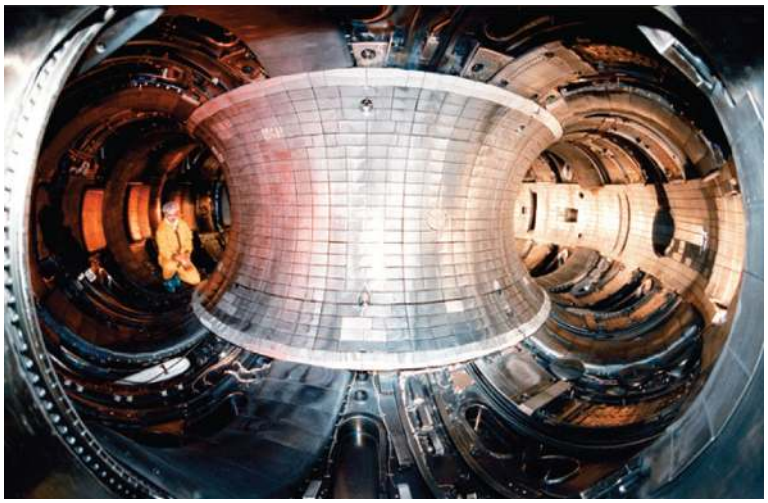


Figure 19.8.2: A Possible Design for a Nuclear Fusion Reactor. The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. 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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19.9: 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:

$$^{2}_{1}\mathrm{D} + {}^{3}_{1}\mathrm{T} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n \tag{19.9.1}$$

For this reaction, Δm = – 0.018 88 g mol^{-1} so that ΔH_m = – 1700 GJ mol^{-1}. Although very large quantities of energy are released by a reaction like Equation 19.9.1, 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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19.10: 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 19.10.1).

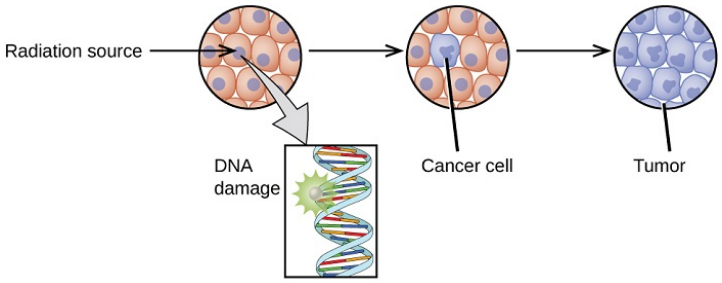


Figure 19.10.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

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 19.10.2).

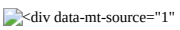


Figure 19.10.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

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:

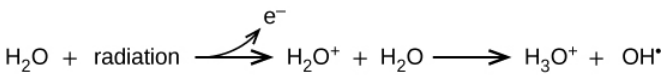


Figure 19.10.3.

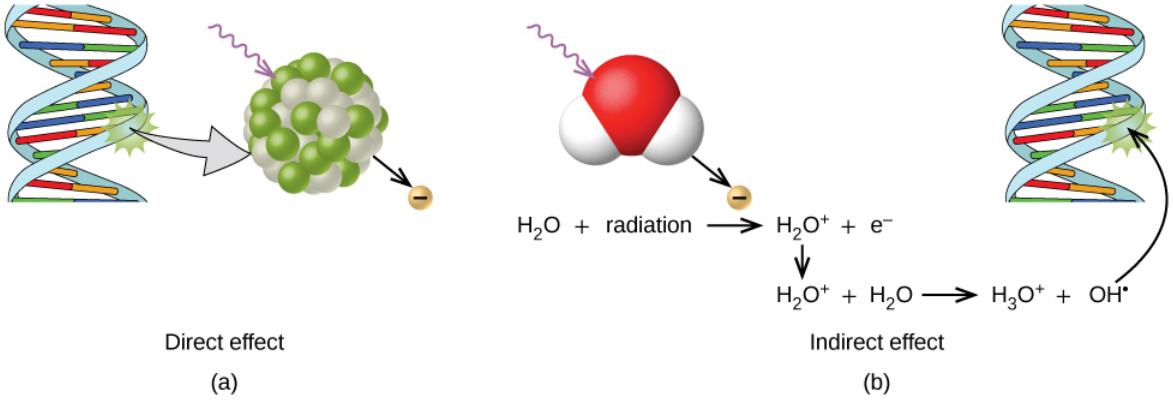


Figure 19.10.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

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 19.10.4). 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.

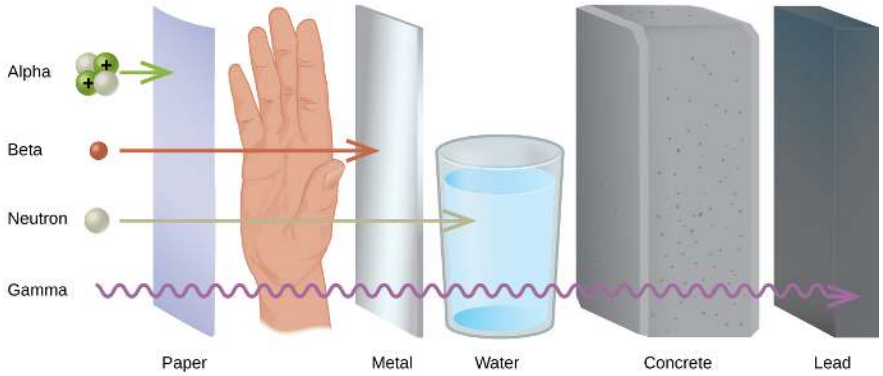


Figure 19.10.4: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

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 19.10.5).

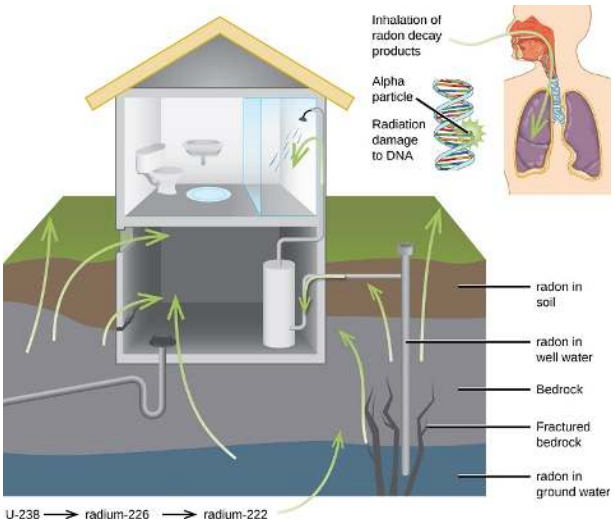


Figure 19.10.5: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

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 19.10.6). 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 19.10.6: 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 19.10.1). 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 = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table 19.10.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for 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:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{19.10.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

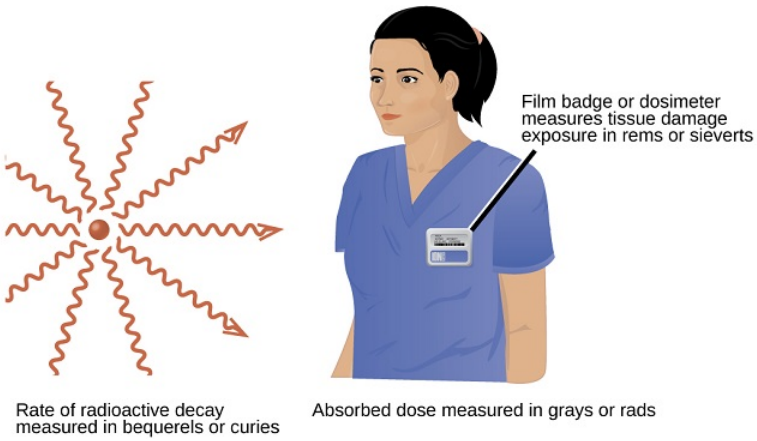


Figure 19.10.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

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 19.10.1: 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 19.10.1

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

$3.56 \times 10^{11}\text{Bq}$

Answer b

$0.962\ \text{Ci}$

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 19.10.8 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).

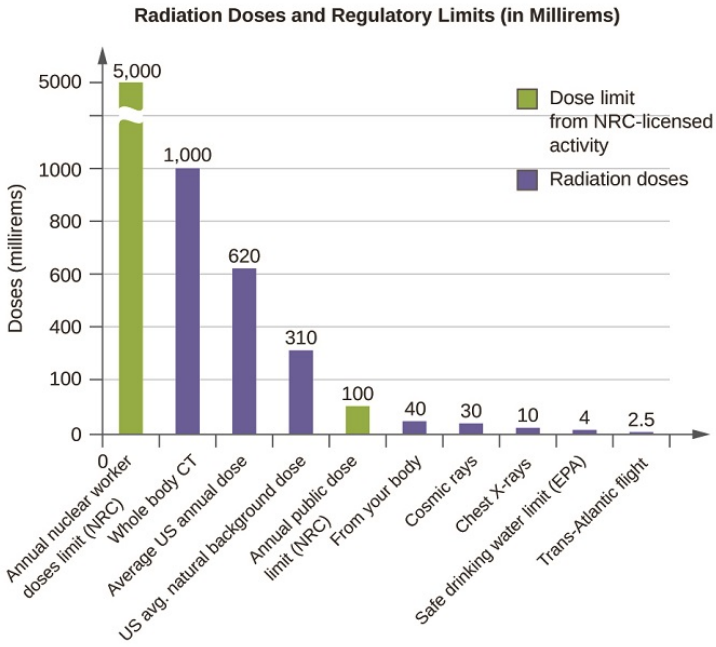


Figure 19.10.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

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 19.10.2

Table 19.10.2: 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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CHAPTER OVERVIEW

20: Organic Chemistry

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20.4: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon
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20.16: Amines
20.17: Polymers

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20.1: What Do I Smell

You have the ability to distinguish thousands of different smells. Some smells can make you hungry, while others make you gag. Sometimes a smell can bring back a distant memory. Do you know what smells are made of? Your eyes sense light, your ears sense sound waves. What is your nose sensing when it smells something?

When you smell something, your nose is sensing many different kinds of molecules. Molecules that smell tend to be small (~1 nanometer or less) and can easily become gases. These molecules can be found in nature or they can be manufactured by chemists. For instance, the molecule vanillin gives vanilla its characteristic smell. Vanillin can either be extracted from vanilla beans or it can be manufactured from coal tar.

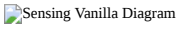
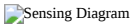


Figure 20.1.1: A molecule of vanillin – grey spheres are carbon, red – oxygen, white – hydrogen. (CC BY-AS 4.0; MRSEC Education Group)

Inside of your nose are nanoscale sensors that can detect these very small smell molecules. Cells called olfactory receptor neurons allow us to smell. “Olfactory” is a word that means related to sense of smell. Inside the cell membranes of the olfactory receptor neurons are odor receptor proteins of several different shapes. Smell molecules have shapes that fit the odor receptor proteins, much like two puzzle pieces fit together. When a molecule comes together with a protein, that protein sends a signal to the brain.



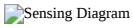


Figure 20.1.2: (left) Odor receptor proteins (purple) are in the cell membranes of olfactory receptor neurons. (right) When a smell molecule fits into the odor receptor protein, it sends a signal to the brain. (CC BY-AS 4.0; MRSEC Education Group)

Most smells are made up of several molecules which activate several different odor receptor proteins. Since there can be many different combinations of signals being sent, the number of smells we can distinguish is far greater than the number of odor receptor proteins. Suppose there was an organism with three types of odor receptor proteins, how many potential smells could it distinguish?

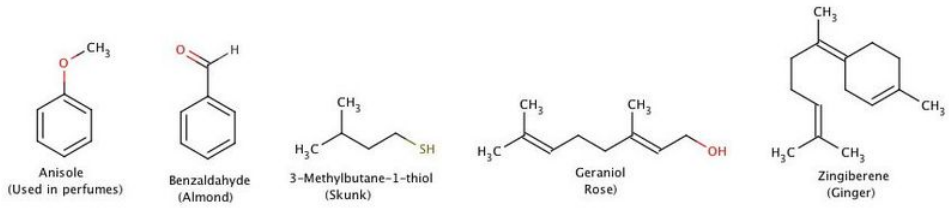


Figure 20.1.3: Different order receptor molecules. (CC0; C5perez via Wikipedia)

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20.2: Vitalism- the Difference Between Organic and Inorganic

Vitalism was a popular philosophical doctrine that posits that living organisms are fundamentally different from non-living entities because they are governed by a "vital force" or "life principle" that cannot be explained solely by physical or chemical processes. This vital force is thought to imbue living beings with qualities such as growth, reproduction, and metabolism, which are not present in inanimate matter.

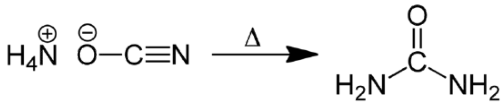
Historically, vitalism was a dominant theory in biology and medicine. Proponents believed that the processes of life could not be understood through the laws of physics and chemistry alone. However, with the advancement of molecular biology, biochemistry, and genetics in the 19th and 20th centuries, vitalism has largely been discredited in the scientific community. Modern science explains the functions and behaviors of living organisms through biochemical and physical principles without invoking a separate vital force. Nonetheless, vitalism has influenced various holistic and alternative medicine practices, where it remains a philosophical underpinning.

Organic vs. Inorganic

The term "organic" in organic chemistry originally derives from the notion that these compounds were fundamentally related to life, or "organisms." In the early days of chemistry, substances were broadly classified into two categories: inorganic and organic. Inorganic substances were those found in the mineral world, while organic substances were associated with living organisms, including plants and animals.

The belief in vitalism posited that organic compounds could **only** be synthesized by living organisms through a "vital force," reinforced the idea that organic compounds were inherently linked to life processes. Compounds such as urea, sugars, fats, and proteins, which were derived from living organisms, were classified as organic. This classification implied that such substances were fundamentally different from inorganic compounds found in the non-living environment.

The synthesis of urea played a crucial role in disproving vitalism by demonstrating that organic compounds, which were thought to be producible only by living organisms due to a "vital force," could be synthesized from inorganic materials in a laboratory setting. In 1828, the German chemist Friedrich Wöhler accidentally synthesized urea, an organic compound found in urine, from ammonium cyanate, an inorganic substance. Wöhler’s experiment showed that organic molecules could be created from inorganic precursors without any "vital force."



Wöhler's synthesis of urea bridged the gap between organic and inorganic chemistry. It provided concrete evidence that the same chemical principles applied to both living and non-living matter. The success of Wöhler's experiment challenged the vitalist notion that a special life force was necessary for the formation of organic compounds. It demonstrated that life processes could be explained by the same physical and chemical laws that govern non-living processes. This discovery paved the way for the development of organic chemistry as a robust scientific discipline. It encouraged further research into the chemical processes of life, leading to a better understanding of biochemistry and molecular biology.

Over time, as the understanding of chemistry advanced, the definition of organic chemistry shifted. Today, organic chemistry is defined as the study of carbon-containing compounds, regardless of their origin. This includes not only compounds derived from living organisms but also synthetic compounds made in laboratories.

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20.3: Carbon- A Versitile Atom

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20.4: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon

Learning Objectives

- Identify alkanes, alkenes, alkynes, and aromatic compounds.
- List some properties of 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 **Alkynes** 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*).

Aromatic hydrocarbons have a special six-carbon ring called a *benzene* ring. Electrons in the benzene ring have special energetic properties that give benzene physical and chemical properties that are markedly different from alkanes. Originally, the term *aromatic* was used to describe this class of compounds because they were particularly fragrant. However, in modern chemistry the term *aromatic* denotes the presence of a six-membered ring that imparts different and unique properties to a molecule.

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:

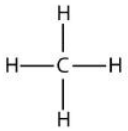


Figure 20.4.1 - Three-Dimensional Representation of Methane.

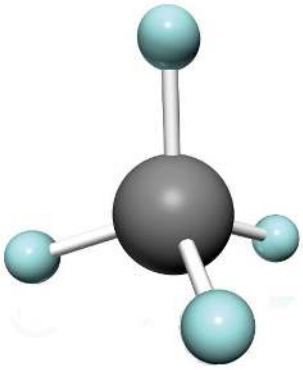
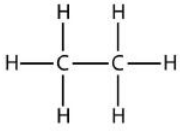
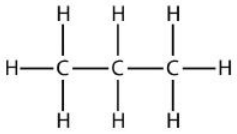


Figure 20.4.1 Three-Dimensional Representation of Methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is C_2H_6, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is C_3H_8:



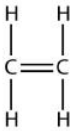
The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is CH_3CH_3, while for propane it is $CH_3CH_2CH_3$. Table 20.4.1 - The First 10 Alkanes, gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

Table 20.4.1 The First 10 Alkanes

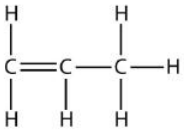
Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$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

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**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are **unsaturated hydrocarbons**. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:

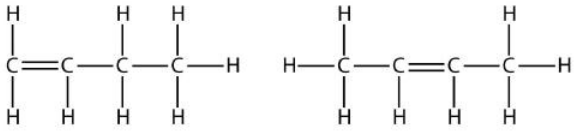


The next largest alkene—propene—has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:



What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms or between the second and third C atoms:



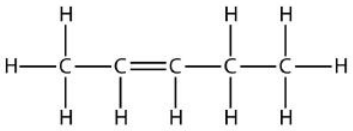
2 structural formulas for butene, with the first butene having the double bond on the first and second carbon from the left and the latter having its double bond on the second and third carbon from the left.

(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.) The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula—C_4H_8. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

Example 20.4.1

Based on the names for the butene molecules, propose a name for this molecule.



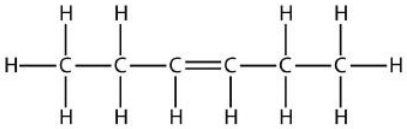
A structural formula of a five carbon molecule with a double bond on the third and fourth carbon from the left. There are ten hydrogen atoms in total.

Solution

With five C atoms, we will use the *pent-* stem, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

Exercise 20.4.1

Based on the names for the butene molecules, propose a name for this molecule.



A structural formula of a six carbon molecule with a double bond on the third and fourth carbon from the left. There are twelve hydrogen atoms in total.

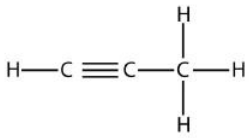
Answer

3-hexene

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne, which is also known as acetylene:

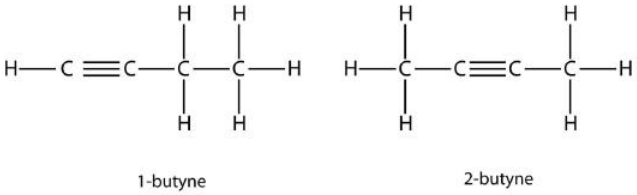


Propyne has the structure



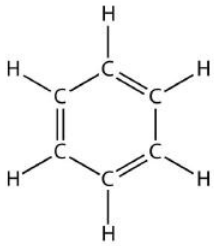
Structural formula showing three carbon molecules with a triple bond present between the first and second carbon atom. The appropriate number of hydrogen atoms is attached to each carbon atom.

With butyne, we need to start numbering the position of the triple bond, just as we did with alkenes:



Two structural formula of butyne. One butyne has a triple bond between the first and second carbon atom, while two butyne has the triple bond between the second and third carbon atom.

Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



The six carbons are arranged in a hexagon pattern with one hydrogen atom emerging outwards from each carbon atom. The presence of a double bond is alternated between every other carbon atom.

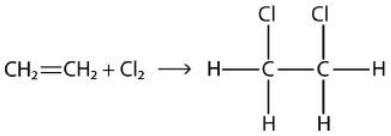
The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as might be suspected. Benzene has the molecular formula C_6H_6; in larger aromatic compounds, a different atom replaces one or more of the H atoms.

As fundamental as hydrocarbons are to organic chemistry, their properties and chemical reactions are rather mundane. Most hydrocarbons are nonpolar because of the close electronegativities of the C and H atoms. As such, they dissolve only sparingly in H_2O and other polar solvents. Small hydrocarbons, such as methane and ethane, are gases at room temperature, while larger hydrocarbons, such as hexane and octane, are liquids. Even larger hydrocarbons are solids at room temperature and have a soft, waxy consistency.

Hydrocarbons are rather unreactive, but they do participate in some classic chemical reactions. One common reaction is substitution with a halogen atom by combining a hydrocarbon with an elemental halogen. Light is sometimes used to promote the reaction, such as this one between methane and chlorine:

$$CH_4 + Cl_2 \overset{light}{\rightarrow} CH_3Cl + HCl$$

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



Structural formula showing the reaction of ethylene with a chlorine molecule to form ethylene dichloride.

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

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

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

By far the most common reaction of hydrocarbons is combustion, which is the combination of a hydrocarbon with O_2 to make CO_2 and H_2O. The combustion of hydrocarbons is accompanied by a release of energy and is a primary source of energy production in our society (Figure 20.4.2 - Combustion). The combustion reaction for gasoline, for example, which can be represented by C_8H_{18}, is as follows:

$$2C^8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O + \sim 5060kJ$$



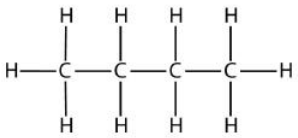
Figure 20.4.2 Combustion © Thinkstock. The combustion of hydrocarbons is a primary source of energy in our society.

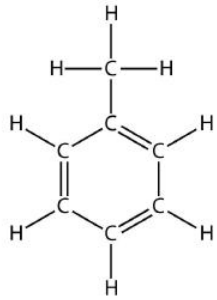
Key Takeaways

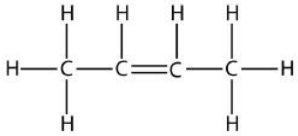
- The simplest organic compounds are hydrocarbons and are composed of carbon and hydrogen.
- Hydrocarbons can be aliphatic or aromatic; aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes.
- The combustion of hydrocarbons is a primary source of energy for our society.

? Exercise 20.4.2

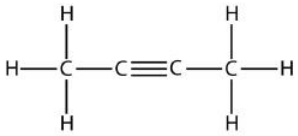
1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

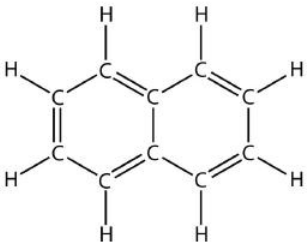
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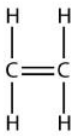
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c. 

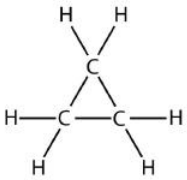
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

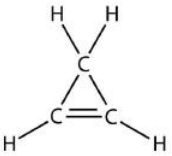
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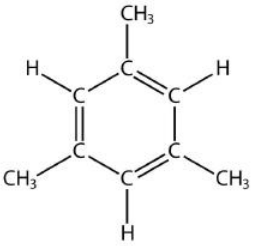
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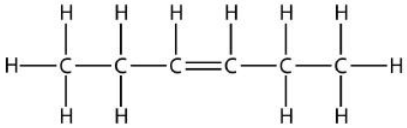
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

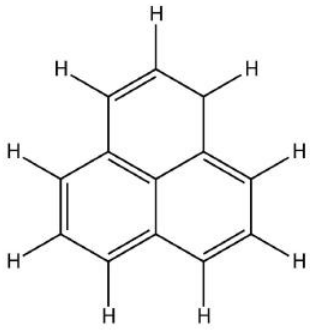
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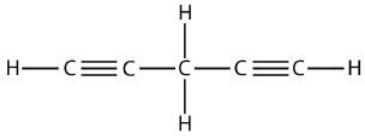
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6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

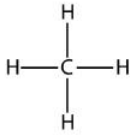
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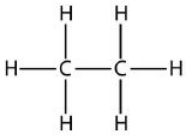
7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why the name *1-propene* is incorrect. What is the proper name for this molecule?
12. Explain why the name *3-butene* is incorrect. What is the proper name for this molecule?
13. Name and draw the structural formula of each isomer of pentene.
14. Name and draw the structural formula of each isomer of hexyne.
15. Write a chemical equation for the reaction between methane and bromine.
16. Write a chemical equation for the reaction between ethane and chlorine.
17. Draw the structure of the product of the reaction of bromine with propene.
18. Draw the structure of the product of the reaction of chlorine with 2-butene.
19. Draw the structure of the product of the reaction of hydrogen with 1-butene.
20. Draw the structure of the product of the reaction of hydrogen with 1-butene.
21. Write the balanced chemical equation for the combustion of heptane.
22. Write the balanced chemical equation for the combustion of nonane.

Answers

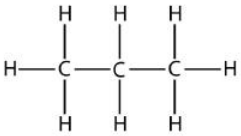
1. an organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons
2.
3. a. aliphatic; alkane
   b. aromatic
   c. aliphatic; alkene
4.
5. a. aliphatic; alkane
   b. aliphatic; alkene
   c. aromatic
6.



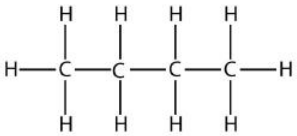
Methane



Ethane

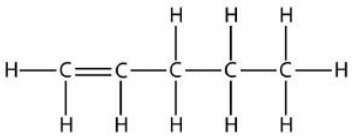


Propane

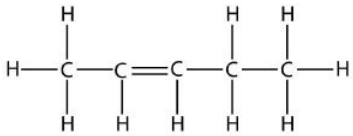


Butane

7.
8.
9. Aromatic means that the molecule has a benzene ring.
10.
11. The 1 is not necessary. The name of the compound is simply *propene*.
12.

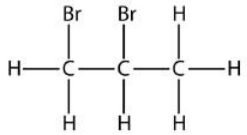


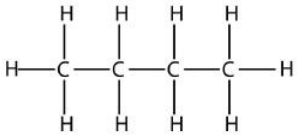
1-Pentene



2-Pentene

13.
14.
15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$
16.

17. 

18.
19. 

20.
21. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

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20.5: Alkanes- Saturated Hydrocarbons

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure 20.5.1.

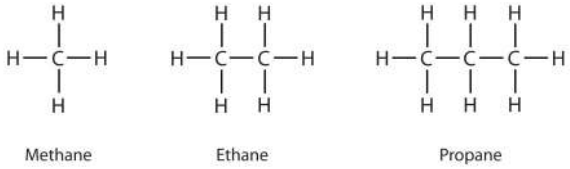


Figure 20.5.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 20.5.2).

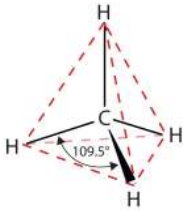


Figure 20.5.2: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 20.5.1.

Table 20.5.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 20.5.3. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

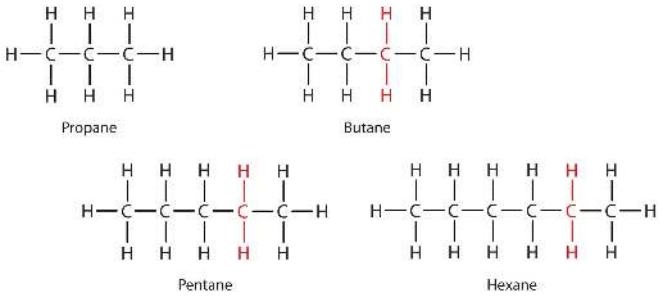


Figure 20.5.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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20.6: Isomers- Same Formula, Different Structure

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20.7: Naming Alkanes

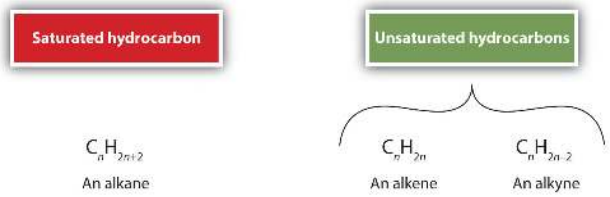
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20.8: Alkenes and Alkynes

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

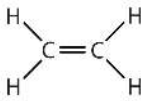


Some representative alkenes—their names, structures, and physical properties—are given in Table 20.8.1.

Table 20.8.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table 20.8.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 20.8.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 20.8.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

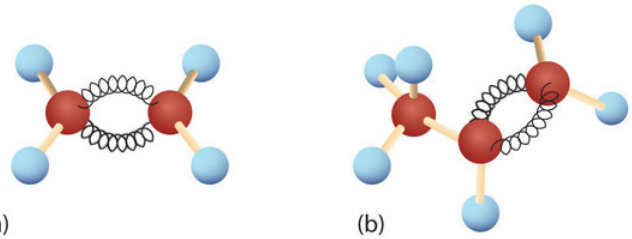
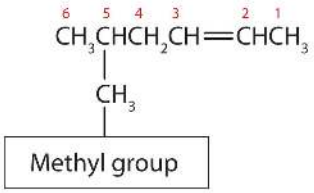


Figure 20.8.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

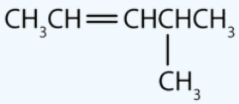
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

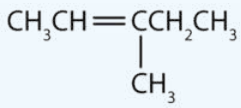
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 20.8.1

Name each compound.

a. 

b. 

Solution

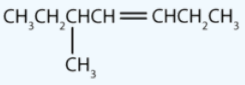
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 20.8.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

Example 20.8.2

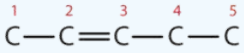
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

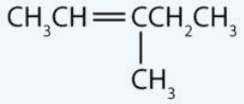
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

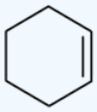


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 20.8.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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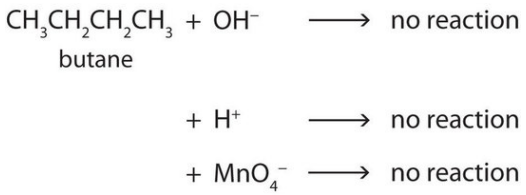
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20.9: Hydrocarbon Reactions

Learning Objectives

- To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:



Butane plus O H superscript negative sign yields no reaction. There is also no reaction of butane with H superscript positive sign and Mn O subscript 4 superscript negative sign.

Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{20.9.1}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{20.9.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{20.9.3}$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

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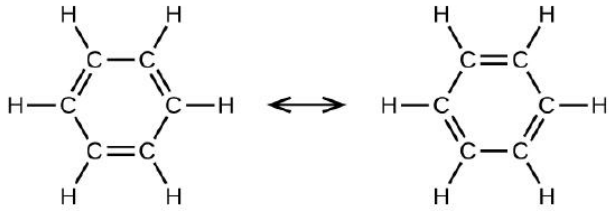
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20.10: Aromatic Hydrocarbons

Textbook, Hydrocarbons

Textbook, Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:



Benzene is shown as a hexagonal ring. There are three double bonds in total. The left structure shows double bonds occupying three sides of the hexagon. A double sided arrow points to the right structure which has three double bonds which occupy the three previously unoccupied sides on the left.

Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized p orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized p orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a $\mathrm{C=C}$ double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 20.10.10

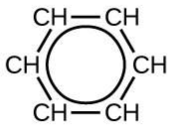
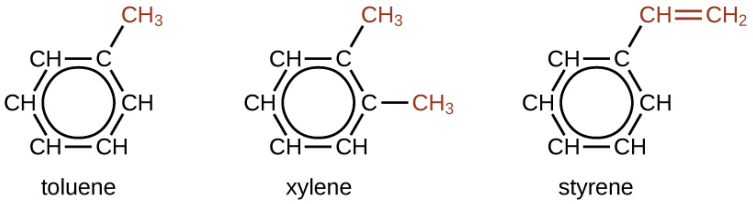


Figure 20.10.10: This condensed formula shows the unique bonding structure of benzene.
A six carbon hexagonal ring structural formula is shown. Each C has an H atom beside it. A circle is at the center of the ring.

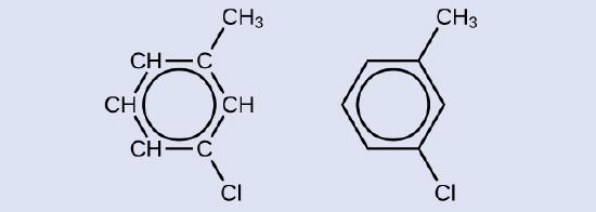
There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:



Toluene has one of the H replaced by C H subscript 3 molecule. Xylene has 2 of the H atoms replaced by two C H subscript 3 molecules respectively. Styrene has one of the H atom replaced C H double bond C H subscript 2.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

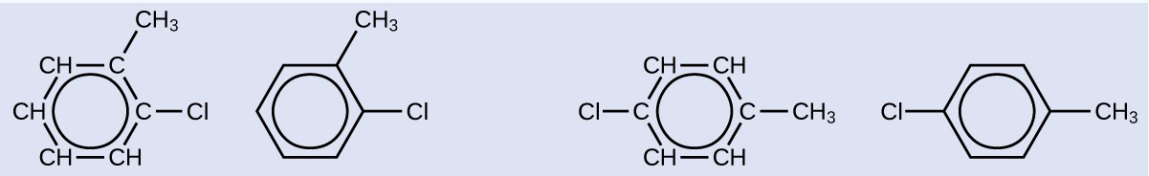
One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



A hexagonal structure of benzene is shown with one of the H replaced by a chlorine atom and another H replaced by C H subscript 3. These two substitutions are apart by 1 carbon atom. Two structures are shown, one shows all the C and H in the ring written out, while the other omits it.

Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:

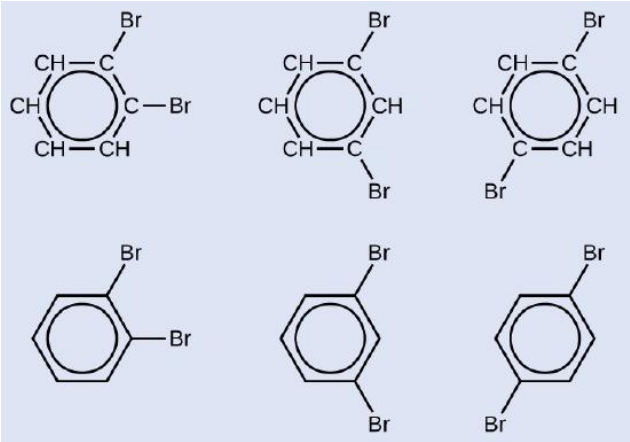


A hexagonal structure of benzene is shown with one of the H replaced by a chlorine atom and another H replaced by C H subscript 3. There are two of these isomers. The first isomer has these two substitutions adjacent to one another while the other are apart by 2 carbons. Two structures are shown for each isomer, one shows all the C and H in the ring written out, while the other omits it.

Exercise 20.10.7

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer



A hexagonal structure of benzene is shown with two of the H replaced by two bromine atoms. Three of these isomers are shown. The first isomer has these two substitutions adjacent to one another, the next isomer has these two bromines 1 carbon apart and the final isomer has two bromines that are two carbons apart. Two structures are shown for each isomer, one shows all the C and H in the ring written out, while the other omits it.

Contributors and Attributions

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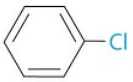
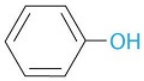
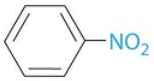
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20.11: Functional Groups

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 20.11.1summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

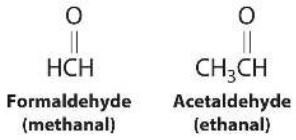
Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO	$CH_3\overset{O}{\overset{\|}{C}}H$	acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	RR′C=O	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	$CH_3\overset{O}{\overset{\|}{C}}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'	$CH_3\overset{O}{\overset{\|}{C}}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′	$CH_3\overset{O}{\overset{\|}{C}}NHCH_3$	*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

[a]R indicates an alkyl group [b]Ar indicates an *aryl* group.

Figure 20.11.1: Major Classes of Organic Compounds

The first family listed in Figure 20.11.1is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 20.11.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para-compounds, the name is meta-xylene or m-xylene.

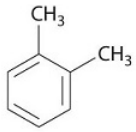
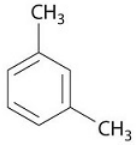
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure 20.11.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

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20.12: Alcohols

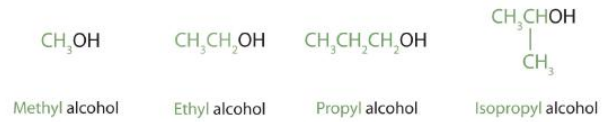
Learning Objectives

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

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*:



Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

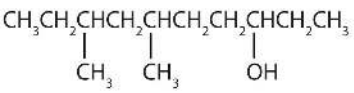
1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Figure 20.12.1shows some examples of the application of these rules.

Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3
Figure 20.12.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Example 20.12.1

Give the IUPAC name for each compound.

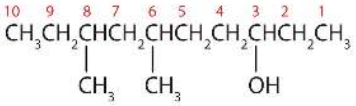
a. 

From left to right, there are ten carbon on the alkane straight chain with methyl groups emerging from carbon 3 and 5 and a hydroxyl group on carbon 8.

- $HOCH_2CH_2CH_2CH_2CH_2OH$

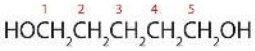
Solution

a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



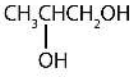
The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH_3) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

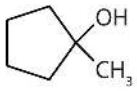
b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



? Exercise 20.12.1

Give the IUPAC name for each compound.

a. 

- 

✔ Example 20.12.2

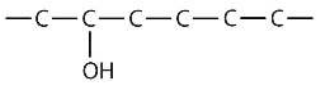
Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

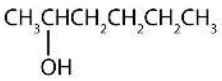
Solution

a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

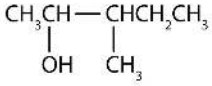
The 2 indicates that the OH group is attached to the second carbon atom.



Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



- The numbers indicate that there is a methyl (CH_3) group on the third carbon atom and an OH group on the second carbon atom.



Exercise 20.12.2

Draw the structure for each compound.

a. 3-heptanol

- 2-methyl-3-hexanol

Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH.



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH.



- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH.

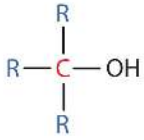
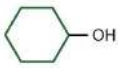


Table 20.12.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Table 20.12.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Summary

In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

Learning Objectives

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O; also written as HOH).



Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 20.12.1).

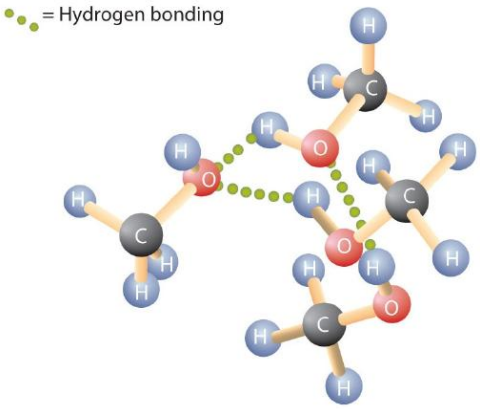


Figure 20.12.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 20.12.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 20.12.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	–164
HOH	water	18	100

Formula	Name	Molar Mass	Boiling Point (°C)
C_2H_6	ethane	30	–89
CH_3OH	methanol	32	65
C_3H_8	propane	44	–42
CH_3CH_2OH	ethanol	46	78
C_4H_{10}	butane	58	–1
$CH_3CH_2CH_2OH$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 20.12.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

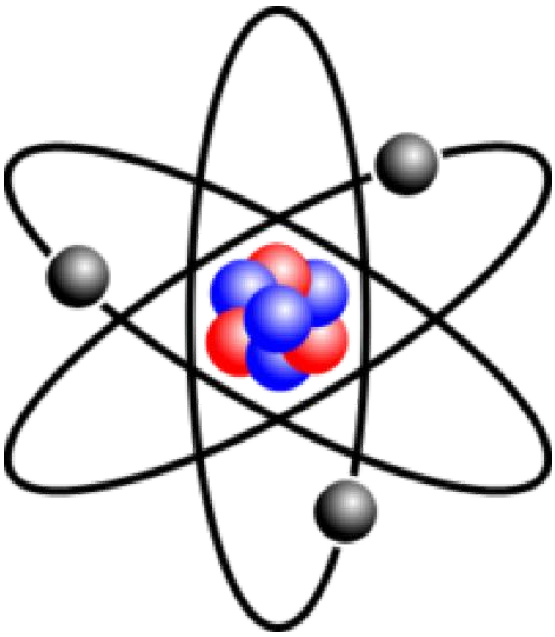


Figure 20.12.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

Learning Objectives

1. Give two major types of reactions of alcohols.
2. Describe the result of the oxidation of a primary alcohol.
3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure 20.12.1, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

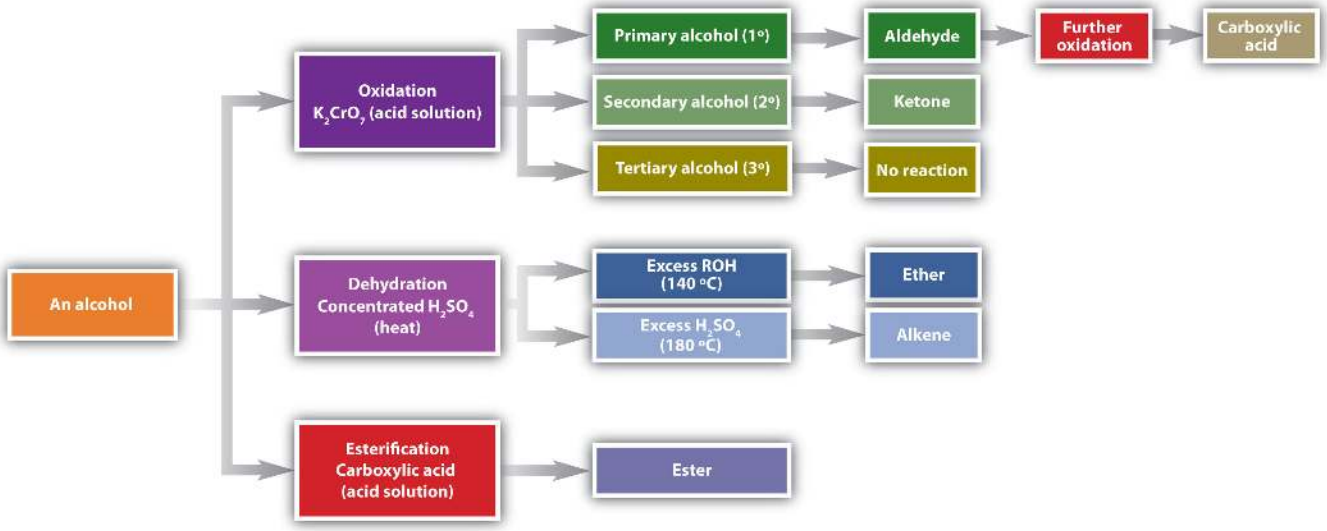
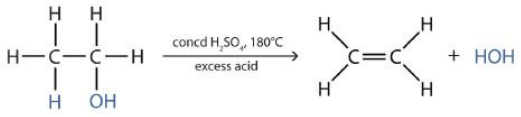


Figure 20.12.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.
A flow diagram of three possible reactions of an alcohol. The final products of the reactions are also shown at the end of the flow diagram.

Dehydration

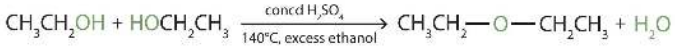
As noted in Figure 20.12.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:



Ethanol Ethylene

Structural formula of ethanol dehydrating under excess concentrated sulfuric acid at 180 degrees celsius. The products are ethylene and a side product of a water molecule.

Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.

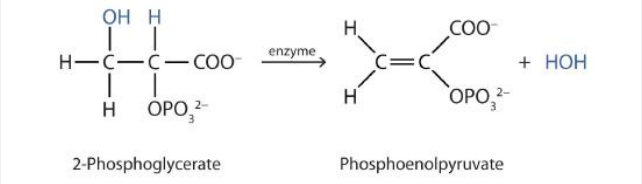


Two molecules of ethanol Diethyl ether

Two molecules of ethanol are dehydrated under concentrated sulfuric acid at 140 degrees celsius and excess ethanol to give a diethyl ether and a water molecule.

(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway

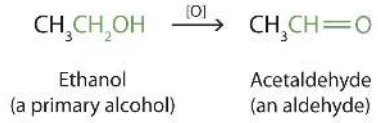


Structural formula of 2 phosphoglycerate forming phosphoenolpyruvate and a water molecule with the aid of enzymes.

Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

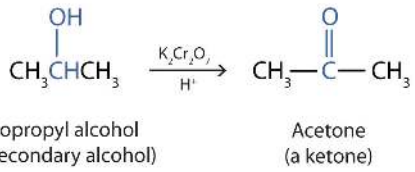
Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:



Formula of ethanol reacting to form acetaldehyde with an O in a bracket above the right pointing arrow.

We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketones*. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:

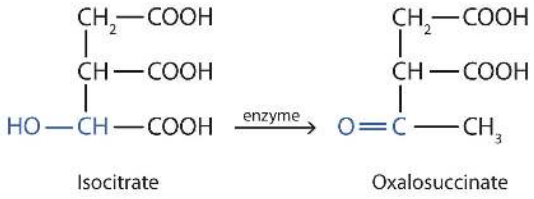


Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:

$$8\,H^{=} + Cr_2O_7^{2-} + 3\,CH_3CH_2OH \longrightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O$$

Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:



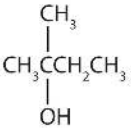
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

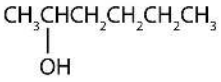
Example 20.12.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

a. $CH_3CH_2CH_2CH_2CH_2OH$

b. 

From left to right, there are four carbons on the alkane straight chain with a methyl and hydroxyl group on carbon 2.

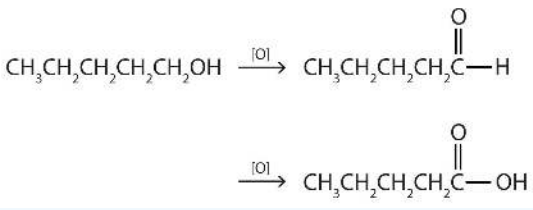
c. 

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

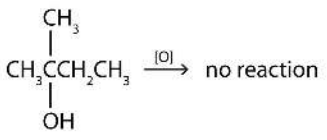
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

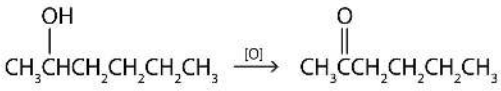
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.

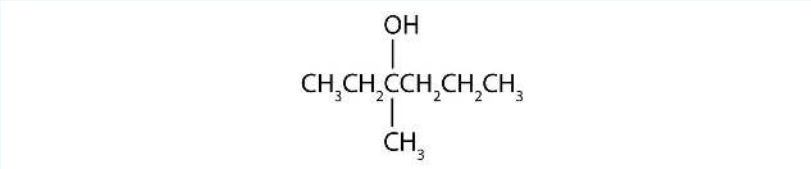


c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.

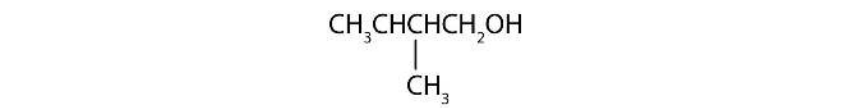


Exercise 20.12.1

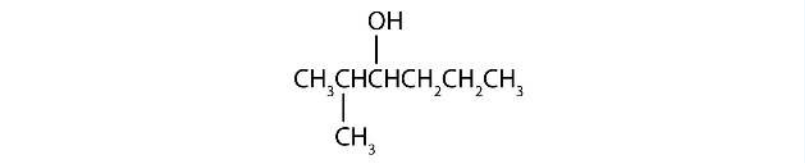
Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

a. 

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group and methyl group on carbon 3.

b. 

From left to right, there are four carbons on the alkane straight chain with a methyl group on carbon 3 as well as a hydroxyl group on carbon 4.

c. 

From left to right, there are six carbons on the alkane straight chain with a methyl group on carbon 2 and a hydroxyl group on carbon 3.

Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

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20.13: Ethers

Learning Objectives

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula ROR′, an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:

$$\mathrm{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \mathrm{ROR'} \xleftarrow[\text{of OH group}]{\text{replace H atom}} \mathrm{ROH}$$

Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, CH_3–O–$CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3–O–CH_3) and diethyl ether CH_3CH_2–O–CH_2CH_3.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 20.13.1).

Table 20.13.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

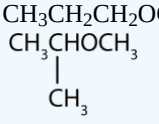
Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Example 20.13.1

What is the common name for each ether?

a. $CH_3CH_2CH_2OCH_2CH_2CH_3$

b. 

Solution

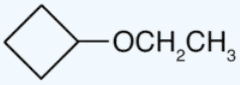
a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.

b. The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether.

Exercise 20.13.1

What is the common name for each ether?

a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$

b. 

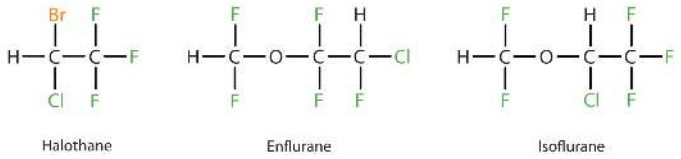
To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

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20.14: Aldehydes and Ketones

Learning Objectives

- Identify the general structure for an aldehyde and a ketone.
- Use common names to name aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.

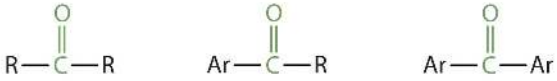
The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.



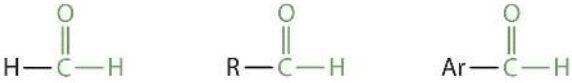
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.*

In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.



In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:



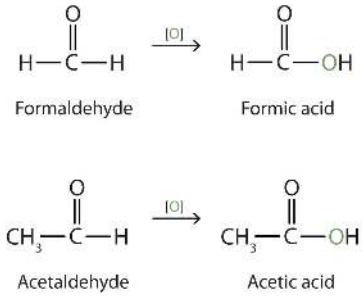
In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O).



The carbon-to-oxygen double bond is not shown but understood to be present. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.

Naming Aldehydes and Ketones

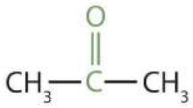
Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.



The stems for the common names of the first four aldehydes are as follows:

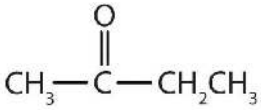
- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



Acetone

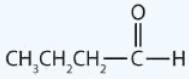
Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

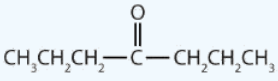


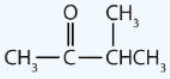
Ethyl methyl ketone

Example 20.14.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

a. 

b. 

c. 

Solution

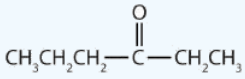
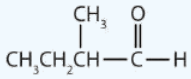
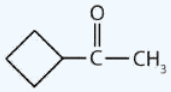
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

Exercise 20.14.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

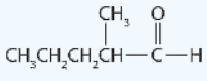
1. 
2. 
3. 

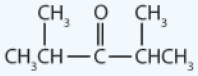
Here are some simple IUPAC rules for naming aldehydes and ketones:

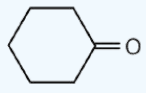
- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
- To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
- To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

Example 20.14.2

Give the IUPAC name for each compound.

a. 

b. 

c. 

Solution

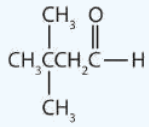
a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.

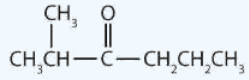
b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.

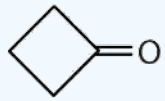
c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

Exercise

Give the IUPAC name for each compound.

a. 

b. 

c. 

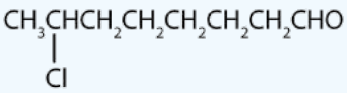
Example 20.14.3

Draw the structure for each compound.

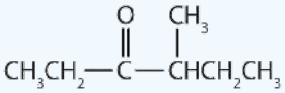
a. 7-chlorooctanal
b. 4-methyl–3-hexanone

Solution

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:



Exercise 20.14.3

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

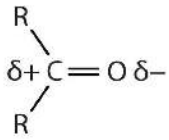
Summary

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:



In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 20.14.1shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

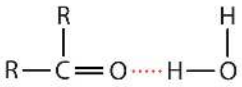
Table 20.14.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	–1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

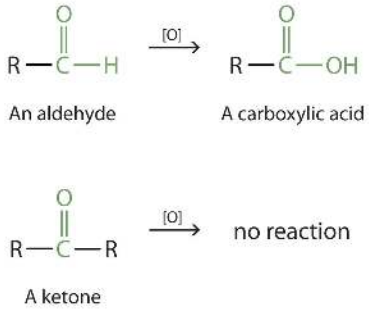
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.



The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.



The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to carboxylic acids.

$$2\,RCHO + O_2 \longrightarrow 2\,RCOOH$$

The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver (Ag^+) ion complexed with ammonia (NH_3), which keeps the Ag^+ ion in solution.

$$H_3N—Ag^+—NH_3$$

When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).

$$\underbrace{RCHO(aq)}_{\text{an aldehyde}} + 2\,Ag(NH_3)_2^+(aq) \longrightarrow RCOO^- + \underbrace{2\,Ag(s)}_{\text{free silver}} + 4\,NH_3(aq) + 2\,H_2O$$

Deposited on a clean glass surface, the silver produces a mirror (Figure 20.14.1). Ordinary ketones do not react with Tollens' reagent.



Figure 20.14.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

A person wearing gloves is holding a bunch of ornaments that she has just lifted from a basin containing a solution.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> *The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a "green" herbal odor to shampoos and other products.*

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 20.14.2).

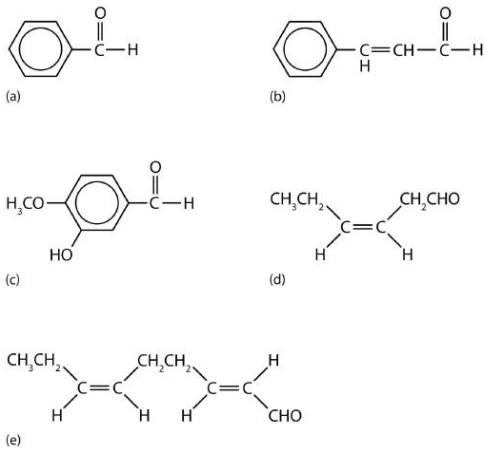


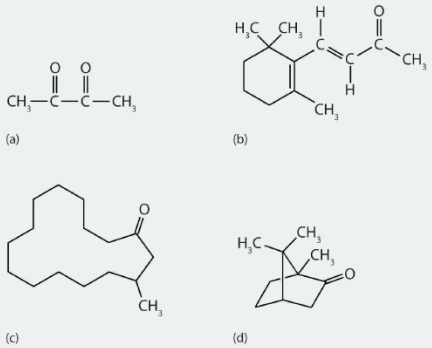
Figure 20.14.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

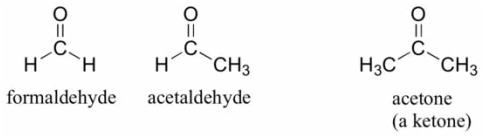
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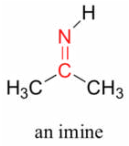
20.15: Carboxylic Acids and Esters

Aldehydes and Ketones

There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.

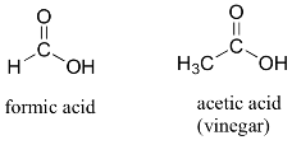


Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.

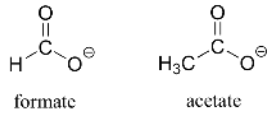


Carboxylic acids and acid derivatives

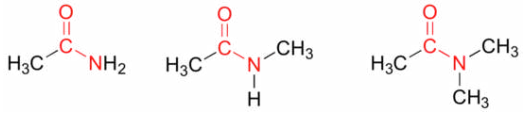
If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives'**, a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.



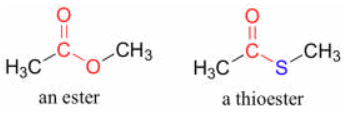
As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).



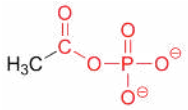
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.

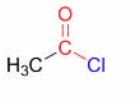


In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.

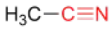


In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.

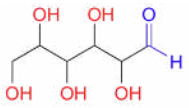

an acyl phosphate

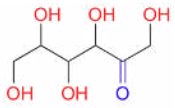

an acid chloride

Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.

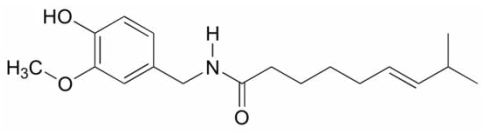

a nitrile

A single compound often contains several functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

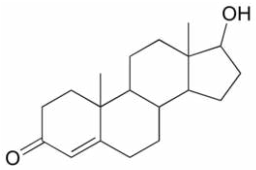

glucose

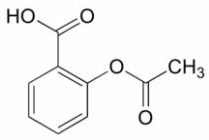

fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.


capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.


testosterone


acetylsalicylic acid
(aspirin)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table on the inside back cover provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

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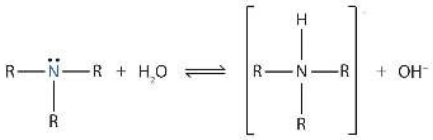
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20.16: Amines

Learning Objectives

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:



As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.

$$\underset{\text{Methylamine}}{CH_3NH_2(aq)} + H_2O \rightleftharpoons \underset{\text{Methylammonium ion}}{CH_3NH_3^+(aq)} + OH^-(aq)$$

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$\underset{\text{Octylamine (insoluble)}}{CH_3(CH_2)_6NH_2(l)} + HNO_3(aq) \longrightarrow \underset{\text{Octylammonium nitrate (soluble)}}{CH_3(CH_2)_6NH_3{}^+NO_3^-(aq)}$$

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

Example 20.16.1

What are the formulas of the acid and base that react to form $[CH_3NH_2CH_2CH_3]^+CH_3COO^-$?

Solution

The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from ethylmethylamine ($CH_3NHCH_2CH_3$). The anion is the acetate ion. It comes from acetic acid (CH_3COOH).

Exercise 20.16.1

What are the formulas of the acid and base that react to form $(CH_3CH_2CH_2)_3NH^+I^-$?

To Your Health: Amine Salts as Drugs

Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as “aniline hydrochloride.” These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

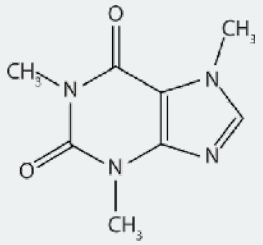
Heterocyclic Amines

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning “other”), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means “like alkalis.” Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

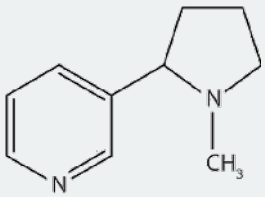
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



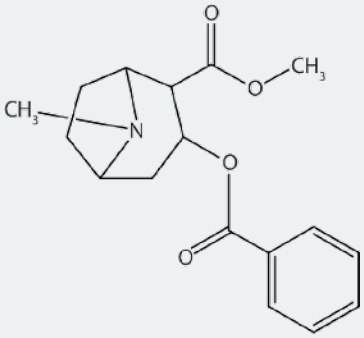
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine’s “high” and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

$$\underbrace{C_{17}H_{21}O_4N}_{\text{cocaine (freebase)}} + HCl \longrightarrow \underbrace{C_{17}H_{21}O_4NH^+Cl^-}_{\text{cocaine hydrochloride}}$$

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

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

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- **15.12: Amines as Bases** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.

20.17: Polymers

Learning Objective

- To understand polymer synthesis.
- To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called polymersA giant molecule that consists of many basic structural units (monomers) connected in a chain or network by covalent bonds. (from the Greek *poly* and *meros*, meaning “many parts”). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses. They consist of basic structural units called monomersThe basic structural unit of a polymer., which are repeated many times in each molecule. As shown schematically in Figure 8.8.1 , polymerizationA process by which monomers are connected into chains or networks by covalent bonds. is the process by which monomers are connected into chains or networks by covalent bonds. Polymers can form via a *condensation reaction*, in which two monomer molecules are joined by a new covalent bond and a small molecule such as water is eliminated, or by an *addition reaction*, a variant of a condensation reaction in which the components of a species AB are added to adjacent atoms of a multiple bond. Many people confuse the terms *plastics* and *polymers*. PlasticThe property of a material that allows it to be molded into almost any shape. is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

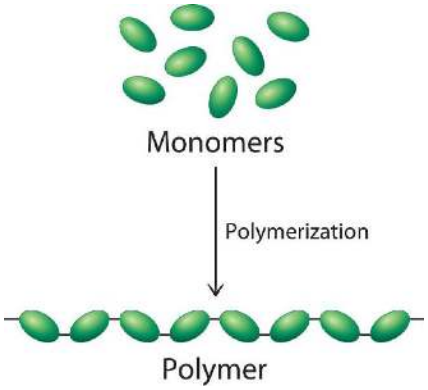


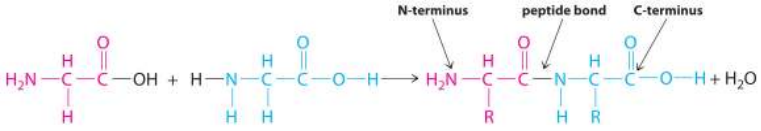
Figure 8.8.1 Polymer formation during a polymerization reaction, *a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

Note the Pattern

Polymers are formed via condensation or addition reactions.

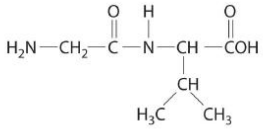
Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where H_2O is eliminated:



In the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-*

terminus). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:



Glycyl-valine

The most important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. Chains with less than about 50 amino acid residues are called peptidesBiological polymers with less than about 50 amino acid residues., whereas those with more than about 50 amino acid residues are called proteinsBiological polymers with more than 50 amino acid residues linked together by amide bonds.. Many proteins are enzymesCatalysts that occur naturally in living organisms and that catalyze biological reactions., which are catalysts that increase the rate of a biological reaction.

Note the Pattern

Synthetic polymers usually contain only a few different monomers, whereas biological polymers can have many kinds of monomers, such as amino acids arranged in different orders.

Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain. Other important peptides are the hormones vasopressin and oxytocin. Although their structures and amino acid sequences are similar, vasopressin is a blood pressure regulator, whereas oxytocin induces labor in pregnant women and milk production in nursing mothers. Oxytocin was the first biologically active peptide to be prepared in the laboratory by Vincent du Vigneaud (1901–1978), who was awarded the Nobel Prize in Chemistry in 1955.

Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion (For more information on corrosion, see Section 17.6.) In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 8.8.2). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibersA particle of a synthetic polymer that is more than 100 times longer than it is wide. that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible –CH_2– units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

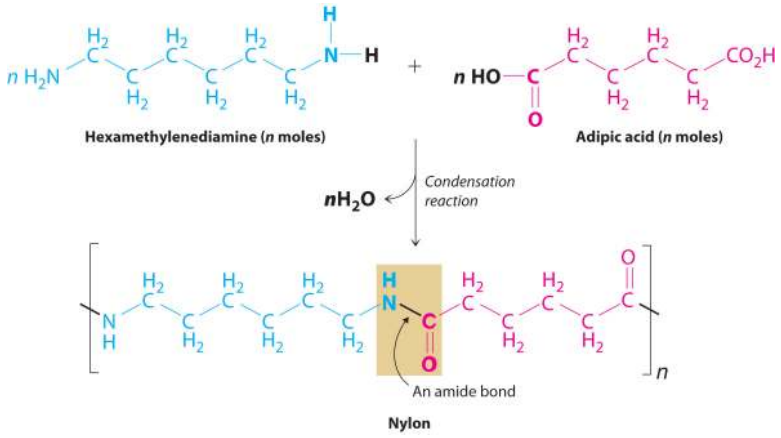
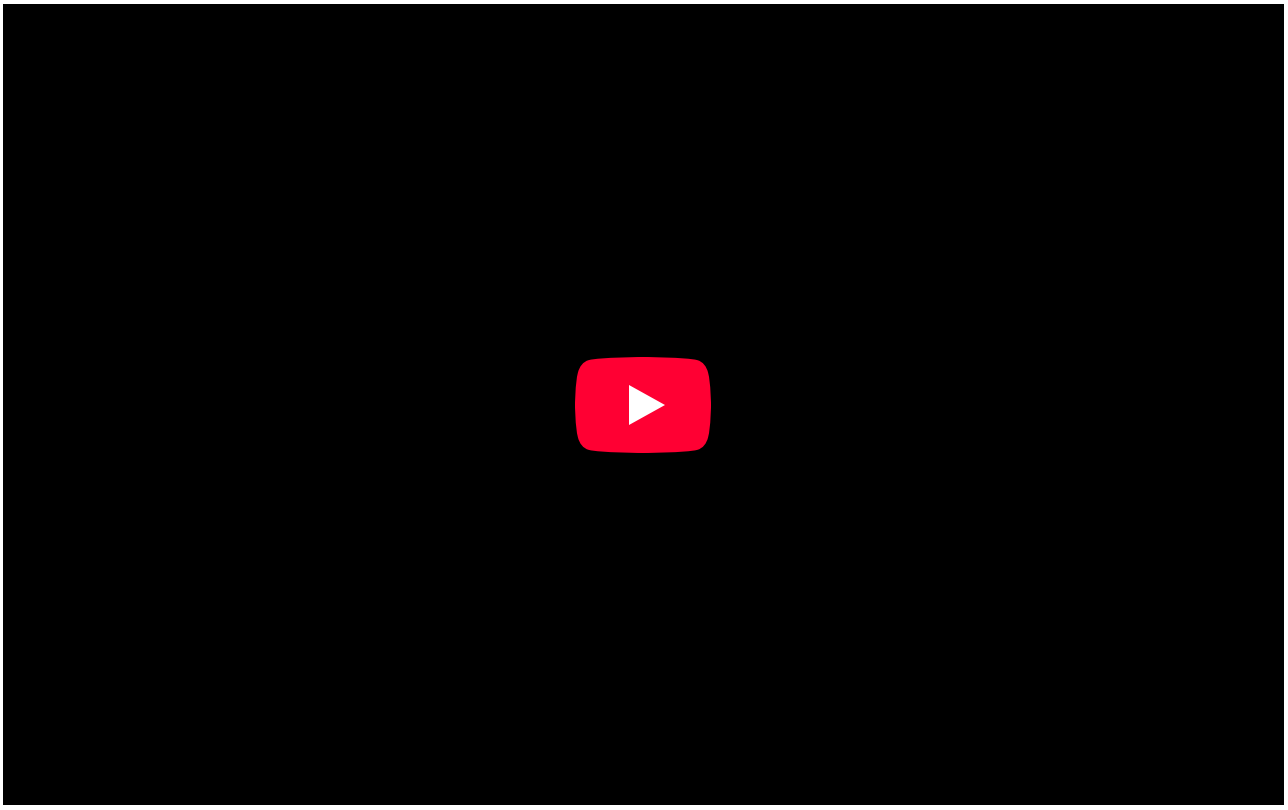


Figure 8.8.2 The Synthesis of Nylon *Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.*

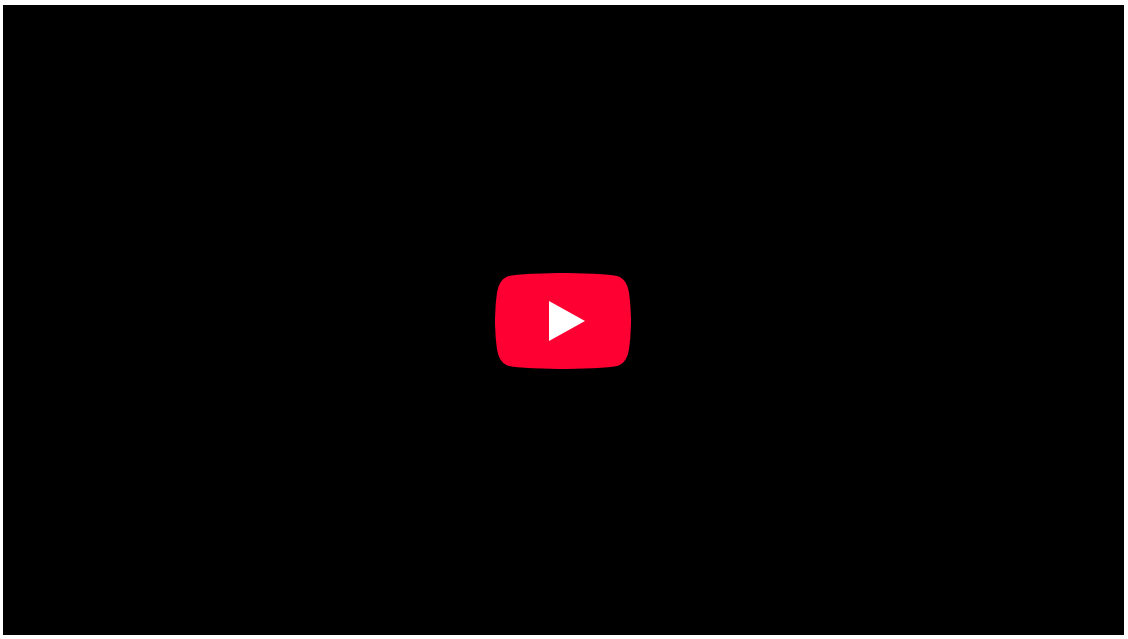


esis of Nylon: *A video showing the synthesis of nylon 6,10* by Mabakken

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel.

Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene (CH_2=CH_2), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene

(LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.



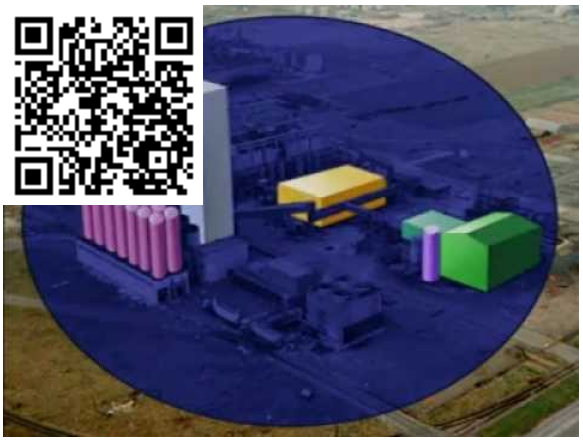


Figure 8.8.4 Commercial Polyethene production: *A video discussing the commercial production of polyethene from the Royal Society of Chemistry*

Because most synthetic fibers are neither soluble nor low melting, multistep processes are required to manufacture them and form them into objects. Graphite fibers are formed by heating a precursor polymer at high temperatures to decompose it, a process called pyrolysisA high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.. The usual precursor for graphite is polyacrylonitrile, better known by its trade name—Orlon. A similar approach is used to prepare fibers of silicon carbide using an organosilicon precursor such as polydimethylsilane $\{[–(CH_3)_2Si–]_n\}$. A new type of fiber consisting of carbon nanotubes, hollow cylinders of carbon just one atom thick, is lightweight, strong, and impact resistant. Its performance has been compared to that of Kevlar, and it is being considered for use in body armor, flexible solar panels, and bombproof trash bins, among other uses.

Because there are no good polymer precursors for elemental boron or boron nitride, these fibers have to be prepared by time-consuming and costly indirect methods. Even though boron fibers are about eight times stronger than metallic aluminum and 10% lighter, they are significantly more expensive. Consequently, unless an application requires boron's greater resistance to oxidation, these fibers cannot compete with less costly graphite fibers.

Example 8.8.1

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

Given: type of polymer

Asked for: application

Strategy:

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

Solution:

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

Exercise

Which products are manufactured from LDPE and which from HPDE?

1. lawn chair frames
2. rope
3. disposable syringes
4. automobile protective covers

Answer

1. HDPE
2. LDPE
3. HDPE
4. LDPE

Summary

Polymers are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

Key Takeaway

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or synthetic polymers.

Conceptual Problems

1. How are amino acids and proteins related to monomers and polymers? Draw the general structure of an amide bond linking two amino acid residues.
2. Although proteins and synthetic polymers (such as nylon) both contain amide bonds, different terms are used to describe the two types of polymer. Compare and contrast the terminology used for the
    1. smallest repeating unit.
    2. covalent bond connecting the units.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Nylon synthesis from MA Bakken @ YouTube

Polyethylene production from Royal Society of Chemistry @ YouTube

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CHAPTER OVERVIEW

21: Biochemistry

21.1: The Human Genome Project
21.2: Proteins
21.3: Protein Structure
21.4: Carbohydrates
21.5: Nucleic Acids- Blueprints for Proteins
21.6: The Cell and Its Main Chemical Components
21.7: Lipids

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21.1: The Human Genome Project

The Human Genome Project was an international scientific research project with the goal of determining the base pairs that make up human DNA, and of identifying, mapping and sequencing all of the genes of the human genome from both a physical and a functional standpoint. It started in 1990 and was completed in 2003.It remains the world's largest collaborative biological project. Planning for the project started after it was adopted in 1984 by the US government, and it officially launched in 1990. It was declared complete on April 14, 2003, and included about 92% of the genome. Level "complete genome" was achieved in May 2021, with a remaining only 0.3% bases covered by potential issues. The final gapless assembly was finished in January 2022.

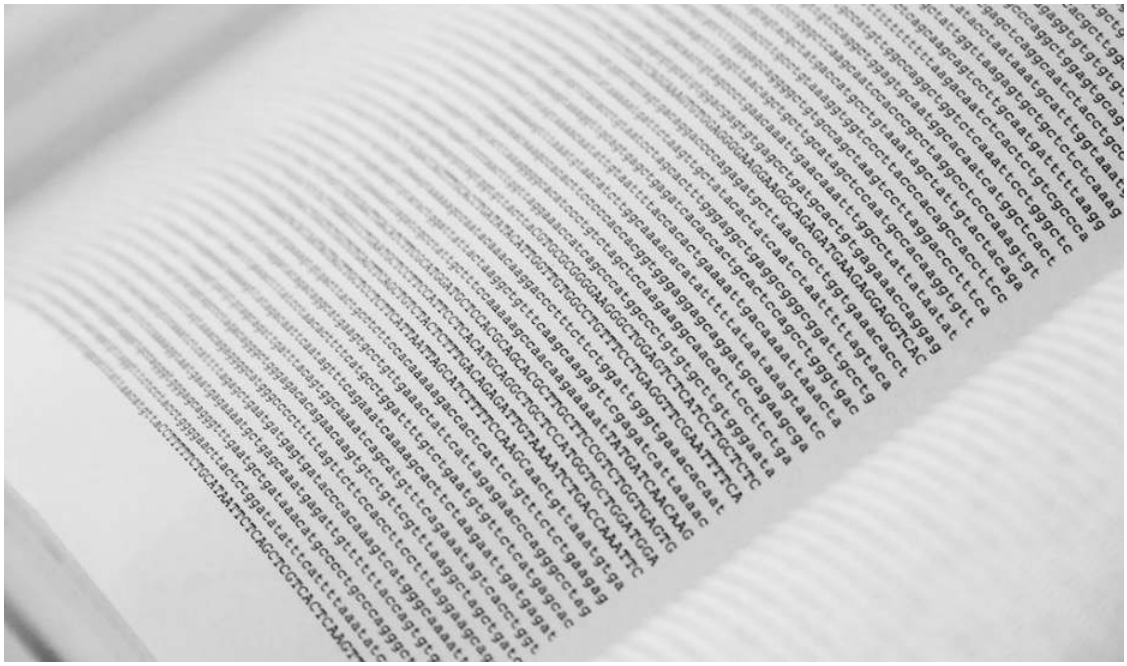


Figure 21.1.1: The Human Genome Project revealed that we are made up of 3.4 billion bases of DNA. The first print out of these are housed in the Wellcome Collection (London) and span over one hundred volumes, each one thousand pages long. This is one of those pages. (CC BY-NC-ND 3.0; Richard Spalding via Flickr)

The sequencing of the human genome holds benefits for many fields, from molecular medicine to human evolution. The Human Genome Project, through its sequencing of the DNA, can help researchers understand diseases including: genotyping of specific viruses to direct appropriate treatment; identification of mutations linked to different forms of cancer; the design of medication and more accurate prediction of their effects; advancement in forensic applied sciences; biofuels and other energy applications; agriculture, animal husbandry, bioprocessing; risk assessment; bioarcheology, anthropology and evolution.

21.1: The Human Genome Project is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

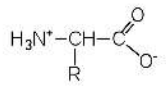
21.2: Proteins

Learning Objectives

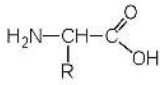
- To recognize amino acids and classify them based on the characteristics of their side chains.

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

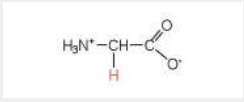
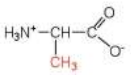
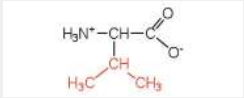
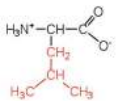


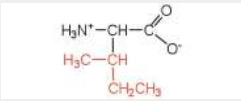
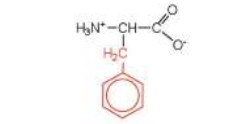
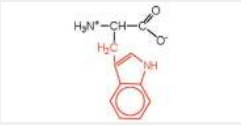
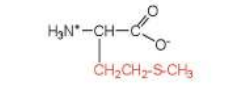
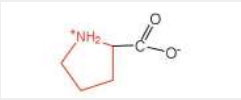
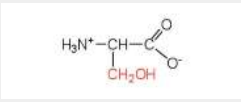
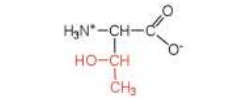
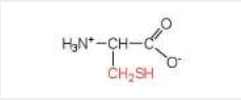
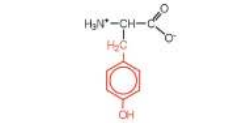
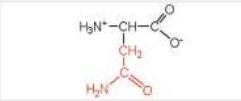
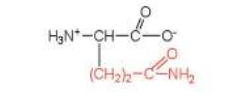
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

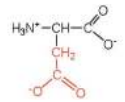
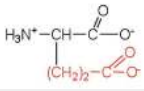
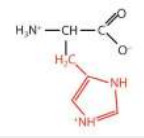
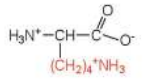
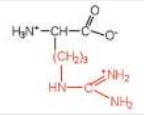
Classification

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 21.2.1.

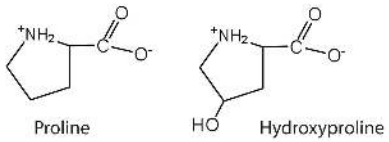
Table 21.2.1: Common Amino Acids Found in Proteins

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

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
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*
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				

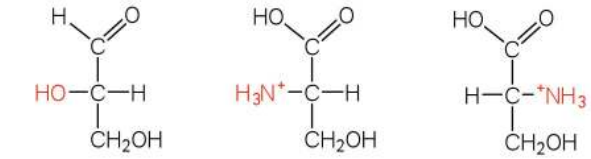
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with 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.



Configuration

Notice in Table 21.2.1 that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

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 what happens when proteins are denatured.
- Identify how a protein can be denatured.

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 21.2.1.

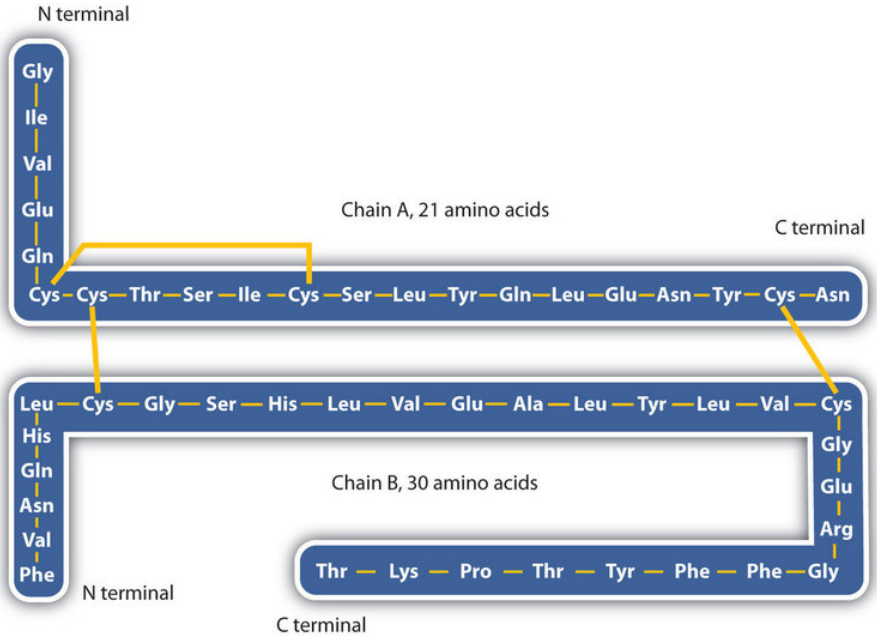


Figure 21.2.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

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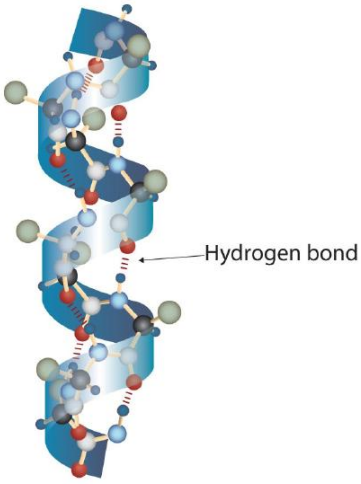


Figure 21.2.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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 21.2.3). 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.

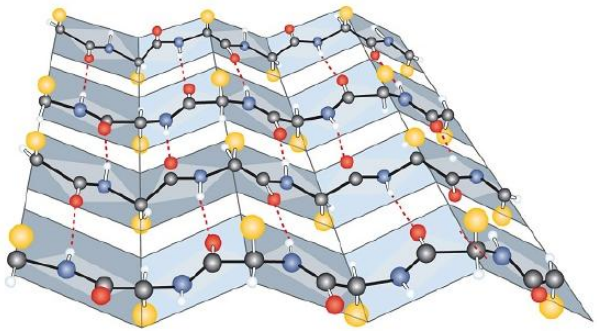


Figure 21.2.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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 21.2.4shows a depiction of the three-dimensional structure of insulin.

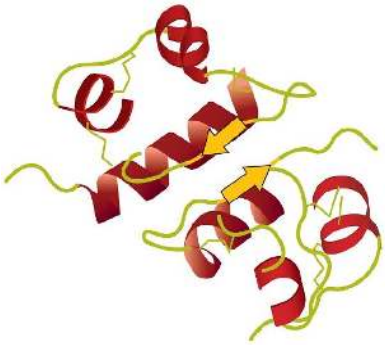
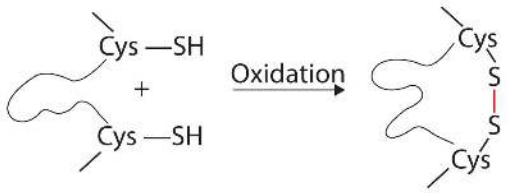


Figure 21.2.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

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 21.2.5).
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 21.2.5).
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 21.2.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 21.2.1) 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 21.2.5). 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.

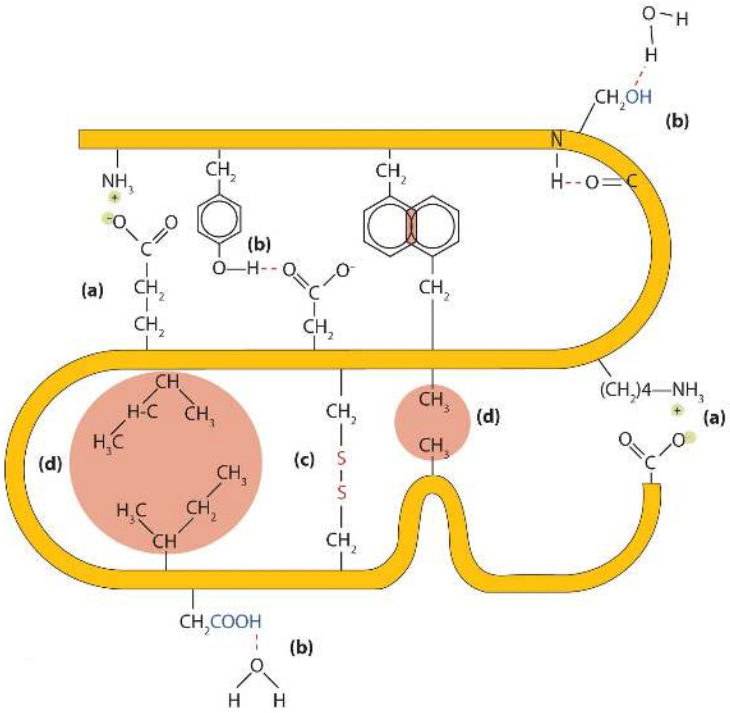


Figure 21.2.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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 21.2.6). 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 21.2.7.



Figure 21.2.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) 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).

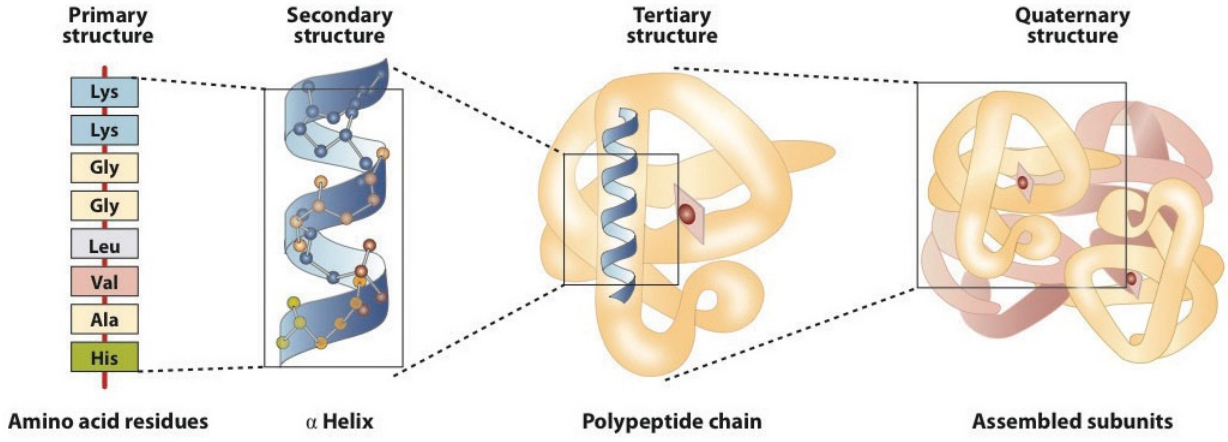


Figure 21.2.7: Levels of Structure in Proteins

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.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 21.2.1).

Figure 21.2.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 21.2.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

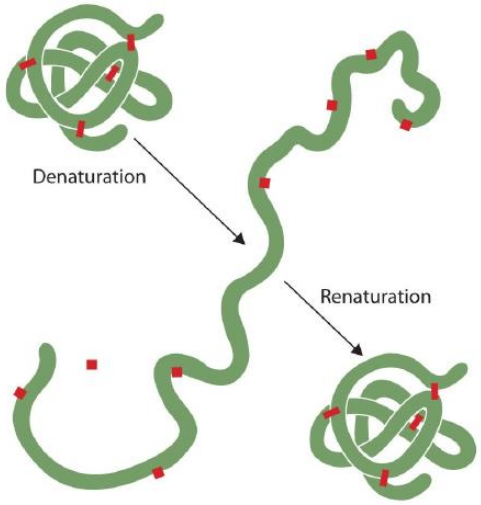


Figure 21.2.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

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. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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21.3: Protein Structure

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- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
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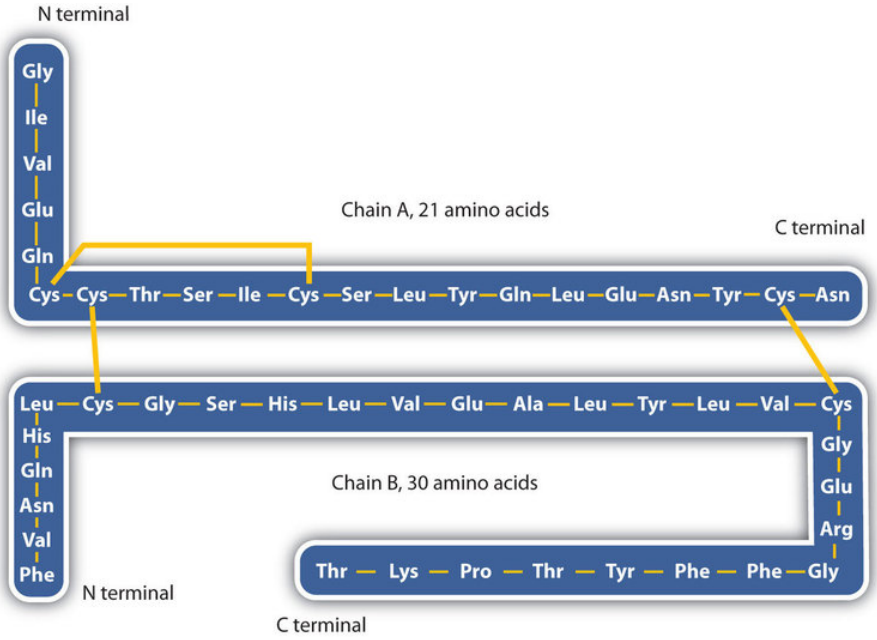


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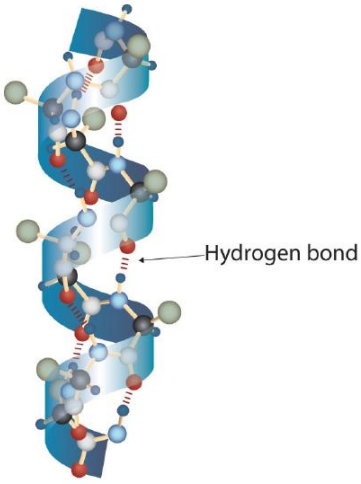


Figure 21.3.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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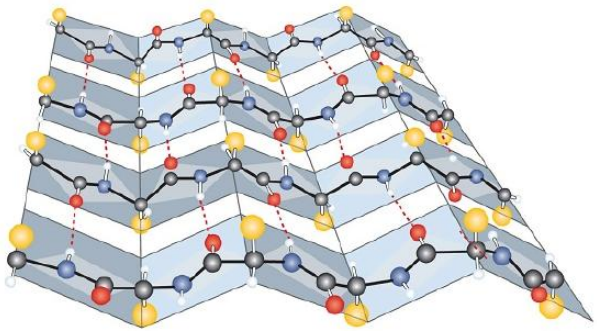


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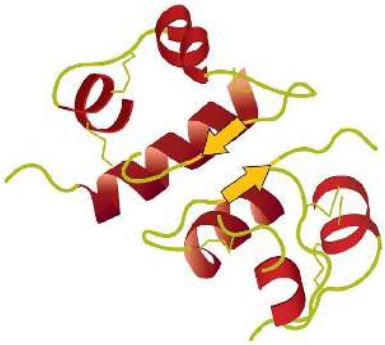
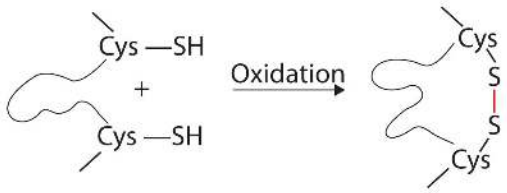


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1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 21.3.5).
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 21.3.5).
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 21.3.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 21.3.1) 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 21.3.5). 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.

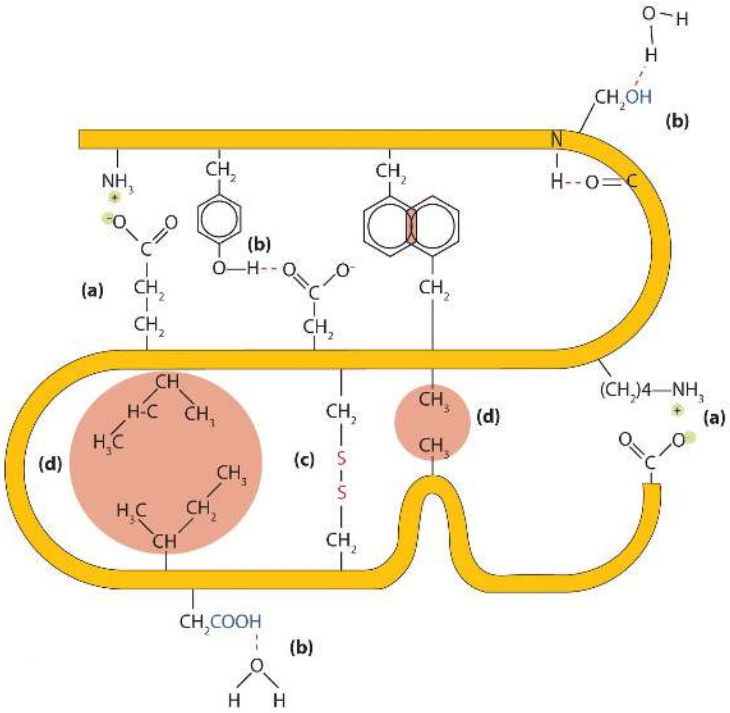


Figure 21.3.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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 21.3.6). 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 21.3.7.



Figure 21.3.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) 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).

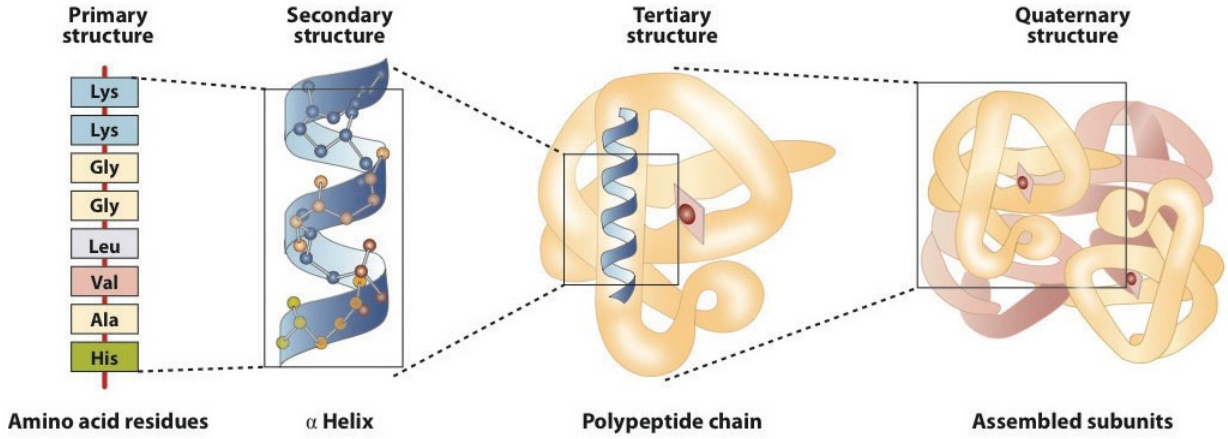


Figure 21.3.7: Levels of Structure in Proteins

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.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 21.3.1).

Figure 21.3.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 21.3.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

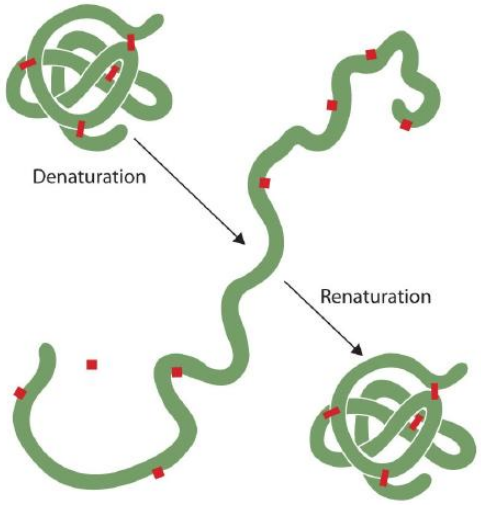


Figure 21.3.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

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. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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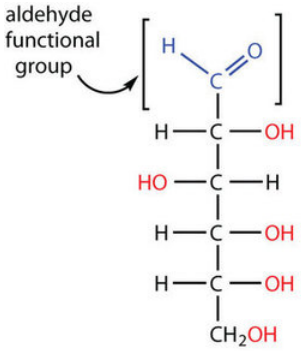
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21.4: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

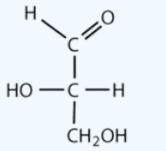
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_6 \cdot 6H_2O$.

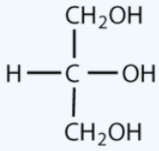


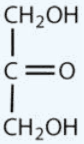
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

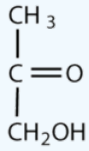
Example 21.4.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

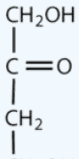
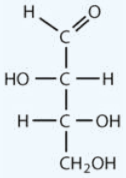
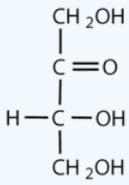
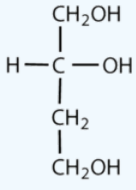
Solution

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 21.4.1

Which compounds would be classified as carbohydrates?

1. 
2. 
3. 
4. 

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:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{21.4.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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21.5: Nucleic Acids- Blueprints for Proteins

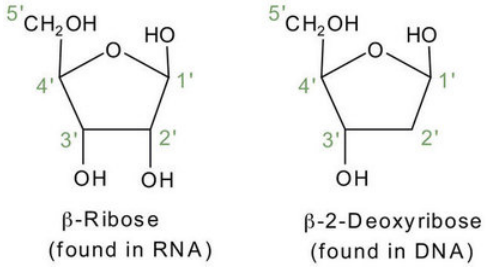
Learning Objectives

- 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 21.5.1).

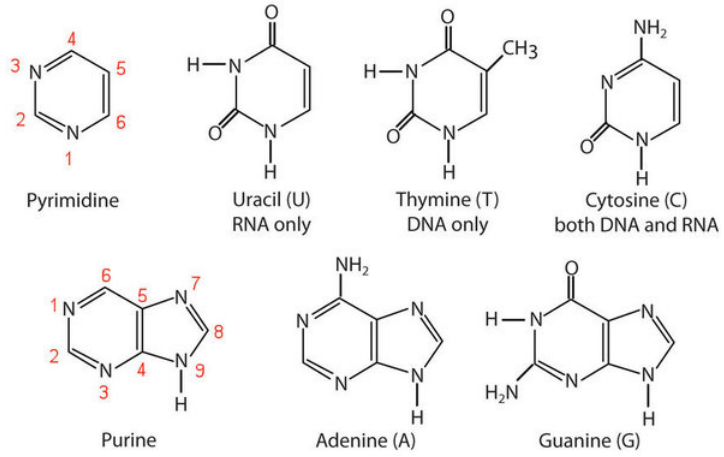


Figure 21.5.1: The Nitrogenous Bases Found in DNA and RNA

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 21.5.1 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 21.5.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	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 21.5.2

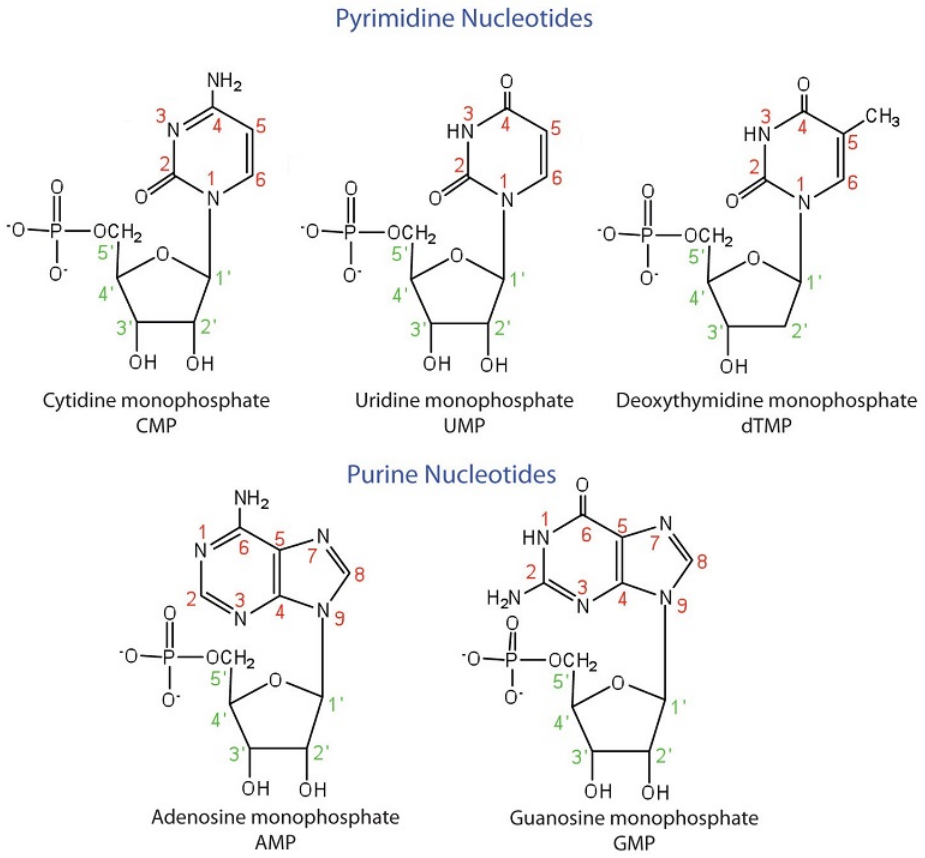


Figure 21.5.2: The Pyrimidine and Purine Nucleotides

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 21.5.3, 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.

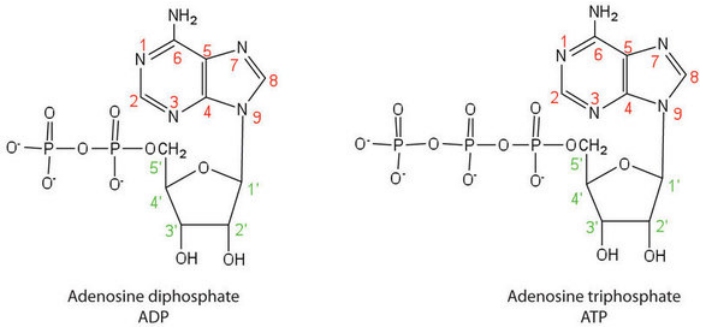


Figure 21.5.3: Structures of Two Important Adenine-Containing Nucleotides

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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21.6: The Cell and Its Main Chemical Components

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21.7: Lipids

On July 11, 2003, the Food and Drug Administration amended its food labeling regulations to require that manufacturers list the amount of *trans* fatty acids on Nutrition Facts labels of foods and dietary supplements, effective January 1, 2006. This amendment was a response to published studies demonstrating a link between the consumption of *trans* fatty acids and an increased risk of heart disease. *Trans* fatty acids are produced in the conversion of liquid oils to solid fats, as in the creation of many commercial margarines and shortenings. They have been shown to increase the levels of low-density lipoproteins (LDLs)—complexes that are often referred to as bad cholesterol—in the blood. In this chapter, you will learn about fatty acids and what is meant by a *trans* fatty acid, as well as the difference between fats and oils. You will also learn what cholesterol is and why it is an important molecule in the human body.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure 21.7.1 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.

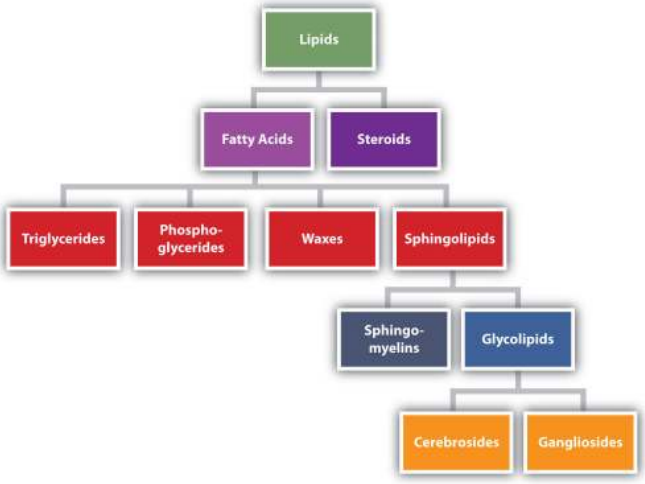


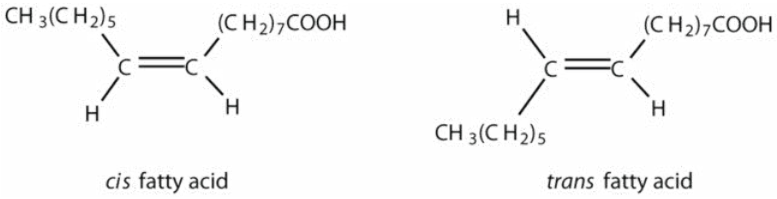
Figure 21.7.1: Lipid Organization Based on Structural Relationships

Lipid categorized into fatty acids and steroids. Fatty acids are further separated into triglycerides, phospho-glycerides, waxes, and sphingolipids. Sphingolipids are separated into sphingo-myelins and glycolipids. Glycolipids are separated into cerebrosides and gangliosides.

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table 21.7.1 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 21.7.1: Some Common Fatty Acids Found in Natural Fats

Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	olive oil
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	−5	canola oil
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	−11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$	−50	liver

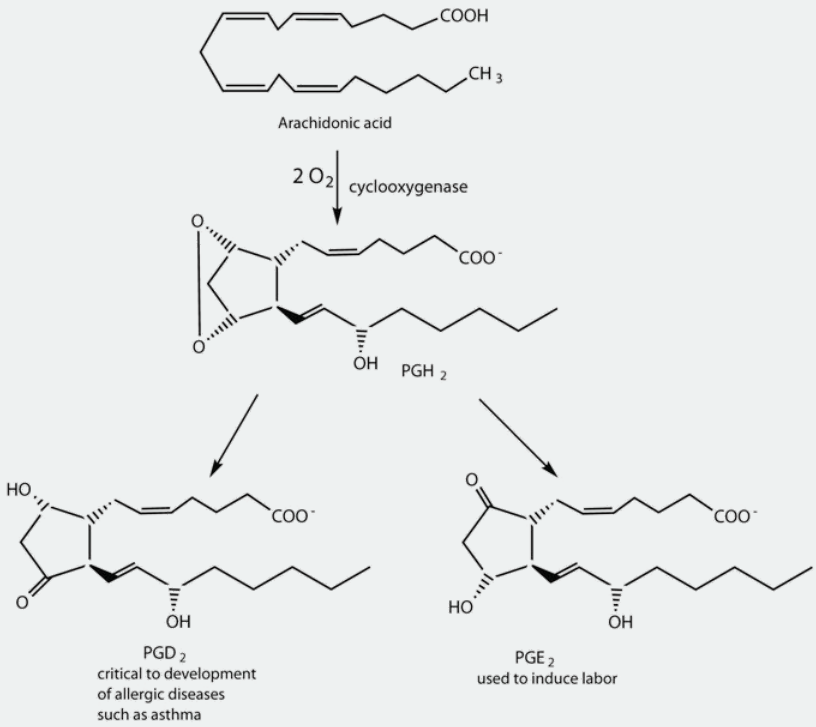
Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the

body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.



Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of PGE_2 are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure 21.7.2*a*). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure 21.7.2*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.

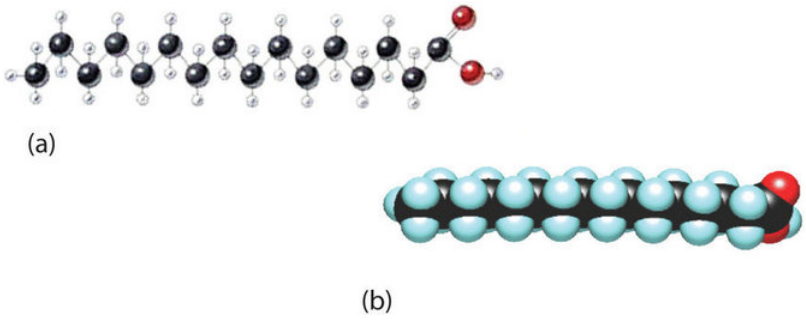
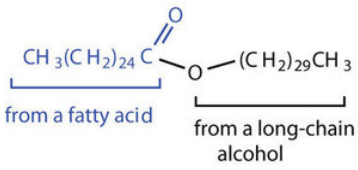


Figure 21.7.2: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Myricyl cerotate
(found in carnauba wax)

Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

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 21.7.1*A*) and animal cells (Figure 21.7.1*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.

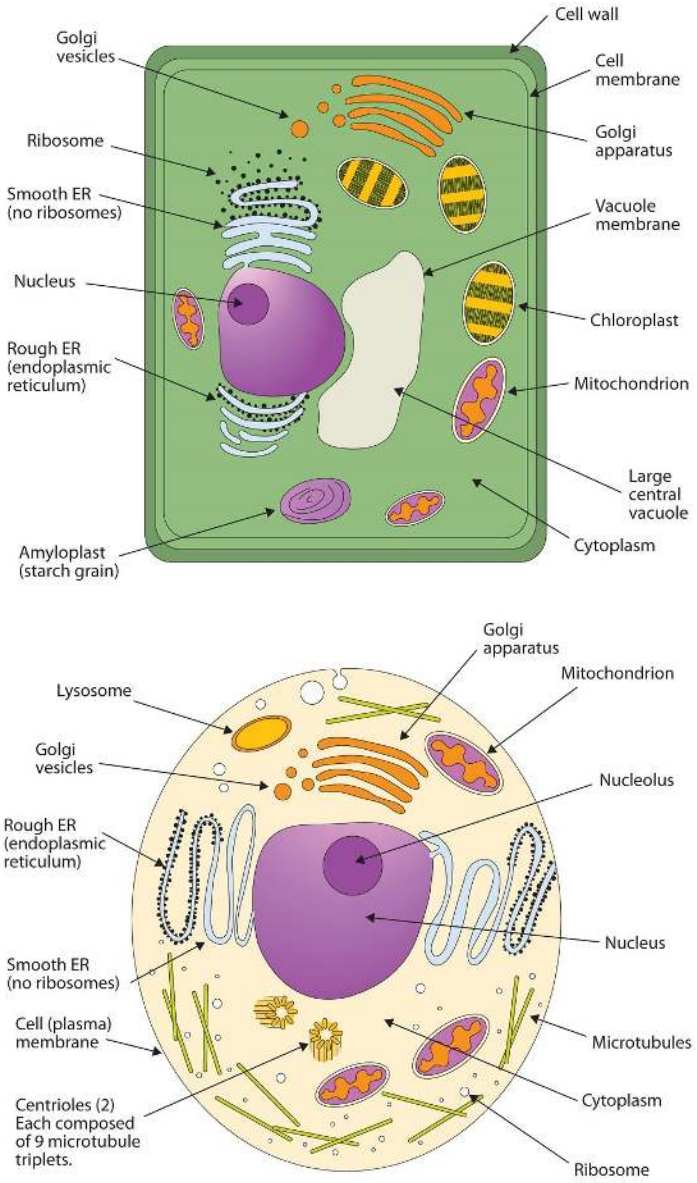


Figure 21.7.1: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

The lipids in cell membranes are highly polar but have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. Often, the ionic part is referred to as hydrophilic, meaning “water loving,” and the nonpolar part as hydrophobic, meaning “water fearing” (repelled by water). When allowed to float freely in water, polar lipids spontaneously cluster together in any one of three arrangements: micelles, monolayers, and bilayers (Figure 21.7.2).

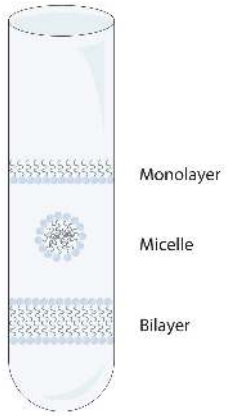


Figure 21.7.2: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

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 21.7.3).

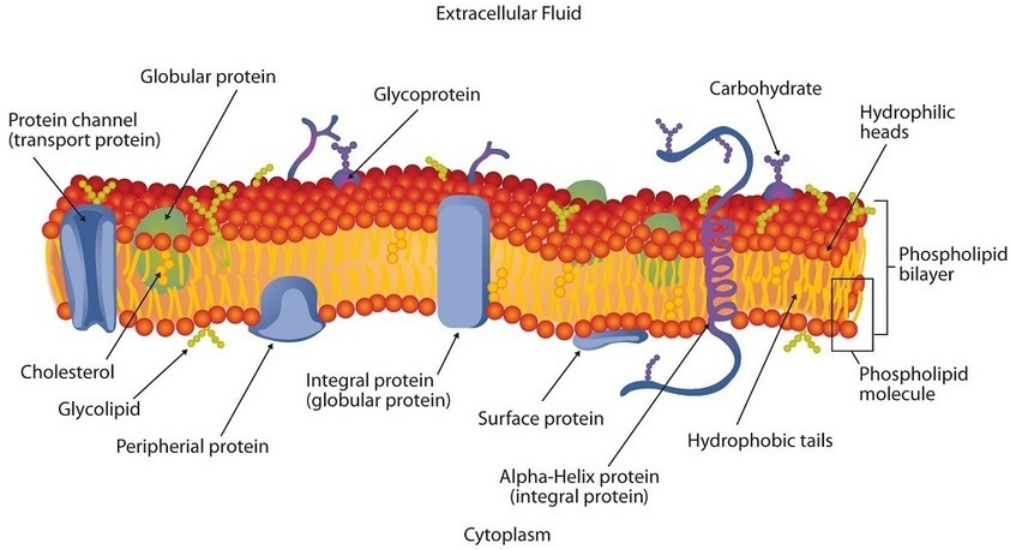


Figure 21.7.3: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of dispersion forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to mill about to some extent, and the membrane is described as fluid.

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 21.7.4

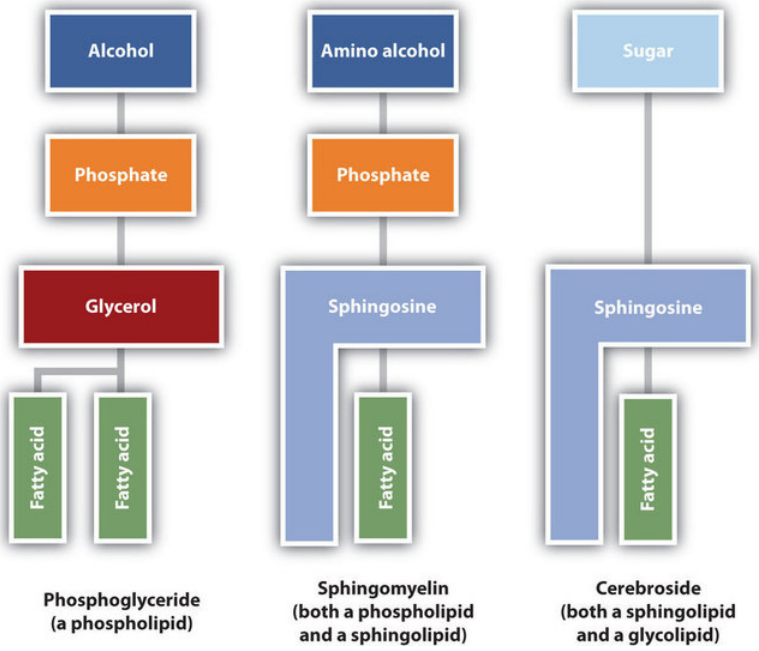


Figure 21.7.4: Component Structures of Some Important Membrane Lipids

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 21.7.5) is attached to the third carbon atom of glycerol (part (b) of Figure 21.7.5). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure 21.7.5).

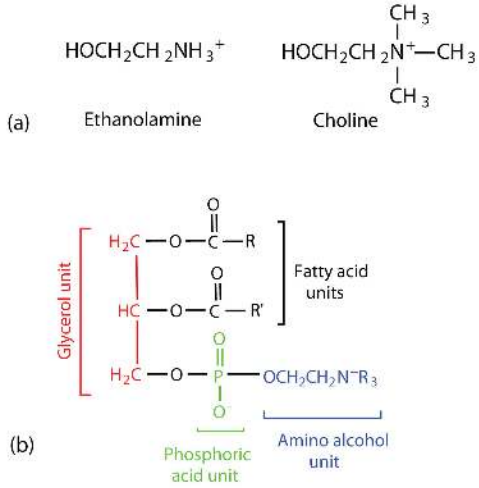
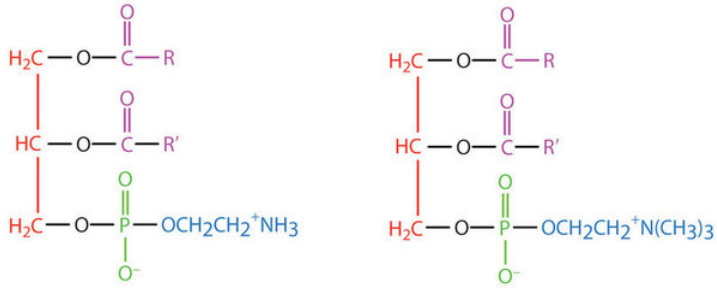


Figure 21.7.5: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

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 21.7.6). 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.

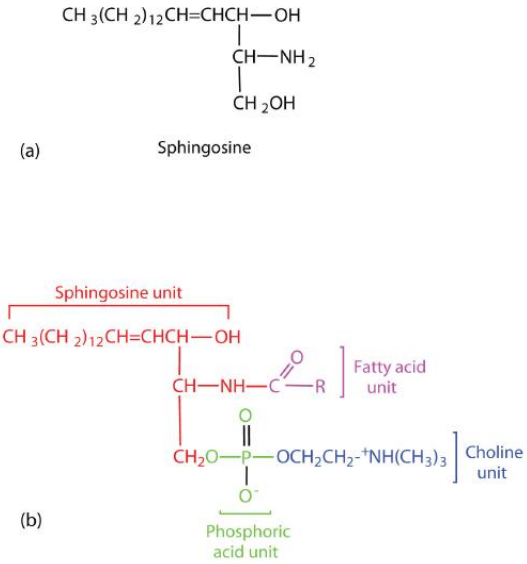


Figure 21.7.6: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

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 21.7.7). 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.

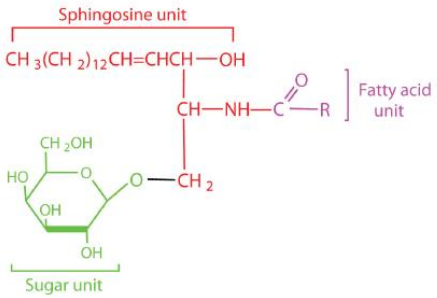


Figure 21.7.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

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 21.7.3). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

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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