CHEMISTRY 110: AN INTRODUCTION TO GENERAL, ORGANIC AND BIOLOGICAL CHEMISTRY



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An Introduction to General, Organic and Biological Chemistry

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Detailed Licensing

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1.1: 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 **1.1.1**: 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 **1.1.1** contains a starter list of common elements that you should begin learning now!

Table **1.1.1**: Names and Chemical Symbols for Common Elements

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

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

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

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

Contributions & Attributions

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1.2: Medicine

How has chemistry made a contributions to medicine?

Diabetes mellitus is a disease characterized by the body's inability to use glucose (a component of table sugar). Glucose is needed to provide biochemical energy for all the cells of the body. When the body cannot make energy using glucose, it begins to break down fat and protein to provide the needed energy, eventually leading to death. Diabetes is the result of the pancreas losing the ability to make insulin, a protein that helps glucose to enter the body's cells and be used for biochemical energy. A key piece of the puzzle surrounding our understanding of diabetes came when Frederick Sanger, a British biochemist, carried out experiments that gave him the structure of the **insulin** molecule. Sanger used basic chemistry techniques and reactions, and took twelve years to complete his research. Today, automated instruments based on his approach can perform the same analysis in a matter of days. Sanger was awarded the Nobel Prize in Chemistry in 1958 for his insulin research.

Chemistry in Medicine

Major contributions to health care have been made by chemistry. The development of new drugs involves chemical analysis and synthesis of new compounds. Many recent television programs advertise the large number of new drugs produced by chemists.

The development of a new drug for any disease is long and complicated. The chemistry of the disease must be studied, as well as how the drug affects the human body. A drug may work well in animals, but not in humans. Out of one hundred drugs that offer the possibility of treating disease, only a small handful actually turn out to be both safe and effective.



Chemistry contributes to the preparation and use of materials for surgery (sutures, artificial skin, and sterile materials). The sutures used in many surgeries today do not have to be removed, because they simply dissolve in the body after a period of time. Replacement blood vessels for heart and other types of surgery are often made of chemicals that do not react with the tissues, so they will not be rejected by the body. Artificial skin can be used to replace human skin for burn patients.



Figure **1.2.2**: *Surgical procedure.* (Courtesy of Mass Communication Specialist 3rd Class Matthew Jackson, U.S. Navy; Source: http://commons.wikimedia.org/wiki/File:Orif_surgery.jpg(opens in new window); License: Public Domain)

Clinical laboratory testing uses a wide variety of chemical techniques and instrumentation for analysis. Clinical laboratory testing allows us to answer commonly asked questions such as "is your cholesterol high?" and "do you have diabetes?" Some laboratory tests use simple techniques. Other processes involve complex equipment and computer analysis data, in order to perform measurements on large numbers of patient samples.



Figure **1.2.3**: *Blood samples for laboratory testing.* (Courtesy of Photographer's Mate 3rd Class Jeremy L. Grisham, U.S. Navy; Source: http://commons.wikimedia.org/wiki/File:US_Navy_060105-N-8154G-010.jpg(opens in new window); License: Public Domain)

Laboratory testing has come to the local drug store or grocery store because of developments in chemistry. You can test your blood glucose using a simple portable device that runs a chemical test on the blood sample and tells you how much glucose is present, allowing a diabetic patient to regulate how much insulin to administer (chemistry is also used to produce the insulin and the disposable syringe that administers the drug).



Figure **1.2.4**: *Blood glucose testing device.* (Courtesy Christopher Tidy (User:Christidy/Wikipedia); Source: http://commons.wikimedia.org/wiki/File:Glucose_meters.jpg(opens in new window); License: Public Domain)



Science Friday: The Medical Wonders of Worm Spit

How useful is worm spit? It turns out that worm spit, also known as silk, is a very useful material in medicine. In this video by Science Friday, Dr. David Kaplan describes how silk is used in a variety of medical applications.



Summary

- Chemistry finds many applications in the healthcare field.
- Development of medicines involves many complicated chemistry processes.
- Chemistry is used to create materials used in surgery.
- Much of laboratory testing is based on chemistry techniques.

Review

1. What chemical is missing in the diabetic patient?
2. Who discovered the structure of insulin?
3. What two things need to be studied to develop a new drug?
4. List two areas where chemistry has helped surgical patients
5. What blood test can be performed using material purchased from your local drugstore?

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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**).

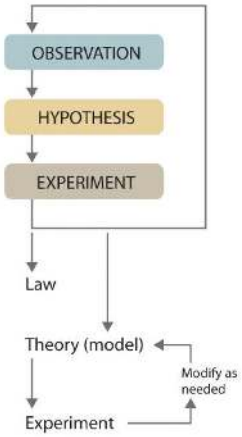


Figure **1.3.1**: The Steps in the Scientific Method.

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.

Contributions & Attributions

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- Wikipedia

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1.4: A Beginning Chemist - How to Succeed

Examples of the practical applications of chemistry are everywhere (Figure **1.4.1**). 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.

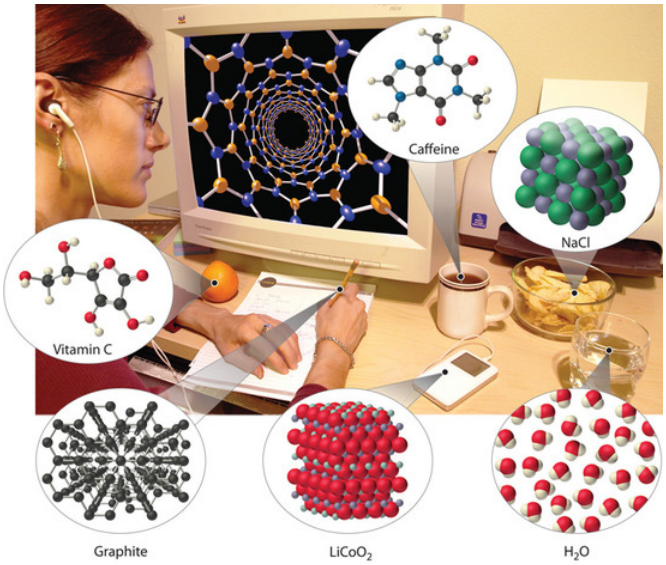


Figure **1.4.1**: Chemistry in Everyday Life. Although most people do not recognize it, chemistry and chemical compounds are crucial ingredients in almost everything we eat, wear, and use.

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 **1.4.1**: How To Study Chemistry.

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1.5: Measurements

Measurements are an essential part of making observations needed to develop science. Several measurements are commonly done in everyday life, as illustrated in Fig. 1.3.1. The measured values have two components: a number and a unit.

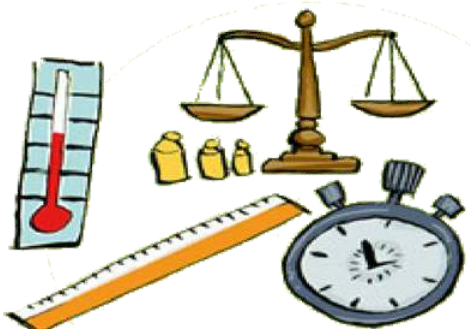


Figure 1.5.1: Measurements of mass, length, time, and temperature are part of daily life. Source: https://www.hiclipart.com/free-trans...xnlrr/download

Numbers

The numbers are composed of digits. The digits are 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9. The digits are written in a row in the number, e.g., 123, which means one hundred and twenty-three. The numbers include a decimal point. If the decimal point is not marked, it is assumed to be present at the right of the number. For example, 123 is 123. by conversion, with the decimal point shown in red font.

Place value of a number

The digits have place values. The place values are relative to the decimal point, i.e., the 1st digit to the left of the decimal point is ones, the 2nd is tens, 3rd is hundreds, and so on. The digit 1st to the right of the decimal point is tenth, 2nd is a hundredth, 3rd is thousandth, and so, as shown in Fig. 1.3.2. For example, in 231.45, the digit 2 is hundreds, i.e., 200, 3 is tens, i.e., thirty, 1 is ones, that is one, 4 is tenth, i.e., four divided by ten, and 5 is hundredth, that is five divided by hundred.

Billions	Hundred millions	Ten millions	Millions	Hundred thousands	Ten thousands	Thousands	Hundreds	Tens	Ones	Decimal place	Tenth	Hundredth	Thousandth	Ten thousandth	Hundred thousandth	Millionth	Ten millionth	Hundred millionth	Billionth	Ten billionth
1	2	3	4	5	6	7	8	9	1	.	1	2	3	4	5	6	8	9	0	1

Figure 1.5.2: Place values of numbers.

Sign of a number

Numbers have signs, either +ve or -ve, to the left of a number, e.g., -23.4 and +430. By conversion, no sign means +ve. The signs are relative to zero; the -ve sign means the number is less than zero, and the +ve sign means the number is more than zero.

The number and the sign in calculations

The rules for the sign in a calculated answer are the following.

1. When two positive numbers add, the answer has a +ve sign, e.g., 3+2 = 5.
2. When two negative numbers add, the answer has –ve sign, e.g., -4 + (-2) = -6.
3. When two numbers having opposite signs add, subtract the smaller number from the larger number, and the answer has the sign of the larger number. For example, -5 +3 = -2.
4. In subtraction, change the sign of the subtracted number and then follow the addition rules. For example, subtract 3 from 5: 5-(+3) = 5-3 = 2. Note that 3 is subtracted, and its sign changed before operating addition. Another example: subtract -6 from 2: 2-(-6) = 2+6 = 8
5. When two positive numbers multiply, the answer has a +ve sign, e.g., 2x3 = 6.
6. When two negative numbers multiply, the answer has a +ve sign, e.g., (-4) x (-3) = 12.
7. When the two numbers multiplied have opposite signs, the answer has a –ve sign, e.g., (-3) x 2 = -6 and 4 x (-4) = -16.
8. When a number is divided by another number, it follows multiplication rules for the sign. For example, $\frac{-4}{-2} = 2,\quad \frac{4}{2} = 2,\quad \frac{-4}{2} = -2,$ and $\frac{9}{-3} = -3.$



Figure **1.5.3**: Battery % remaining.

Percentage calculations

The percentage (%) is the part out of a hundred, as illustrated in Fig. 1.3.3. The percentage is calculated as part divided by the total and then multiplied by a hundred, i.e.:

$$\text{percentage } \% = \frac{\text{Part amount}}{\text{Total amount}} \times 100$$

Example 1.5.1

Calculate the percentage of aspirin if there is 81 mg aspirin in a 325 mg tablet?

Solution

part = 81 mg aspirin, Total = 325 mg tablet

Formula:

$$\text{percentage } = \frac{\text{Part amount}}{\text{Total amount}} \times 100$$

Plug in values in the formula and calculate:

$$\text{Percentage } = \frac{\text{81mg aspirin}}{\text{325mg tablet}} \times 100 = 25\% \text{ aspirin}$$

Example 1.5.2

A piece of 18K green color gold jewelry has 7.5 g gold, 2.0 g silver, and 0.5 g copper. Calculate the percentage of gold in the jewelry?

Solution

Part = 7.5 g gold, Total = 7.5 g gold + 2.0 g silver + 0.5 g copper = 10 g jewelry.

Plug in values in the formula and calculate:

$$\text{percentage } = \frac{\text{Part amount}}{\text{Total amount}} \times 100 = \frac{\text{7.5ggold}}{\text{10 g}} \times 100 = 75\%\text{gold}$$

Writing numbers in scientific notation

Sometimes the given number is too large or too small to be easily written, read, and grasped. Scientific notation is one approach to changing a too large or a too-small number into an easily readable and writable number. The following steps convert a given number to scientific notation.

1. Move the decimal point to the right or the left side, one digit at a time, till the largest non-zero digit becomes one's place.

   For example, move the decimal in 12,700,000 seven times to the right 12,700,000. to obtain 1.27, and move the decimal in 0.000,006 six-time to the left 0.000,006. to get 6. The numbers 1.27 and 6 obtained are the coefficients of the scientific notation.
2. The coefficient is multiplied by 10^x, where x is a power of ten. The power of ten equals the number of times the decimal moved. The sign of the power is +ve if the decimal moved to the left and -ve if the decimal moved to the right. For example, 12,700,000 in scientific notation is 1.27 x 10^7, and 0.000,006 is 6 x 10^{-6}.

Units

Physical properties like mass, length, and temperature are measured. The measured value is a combination of a number and a unit, as illustrated in Fig. 1.3.4. For example, a person's height is 1.83 meters, where 1.83 is a number and a meter is a unit.

> Units are quantities defined by the standard that peoples agree to use as a reference.

For example, the meter is defined as the distance light travels in a vacuum in $\frac{1}{299,792,458}$ of a second.

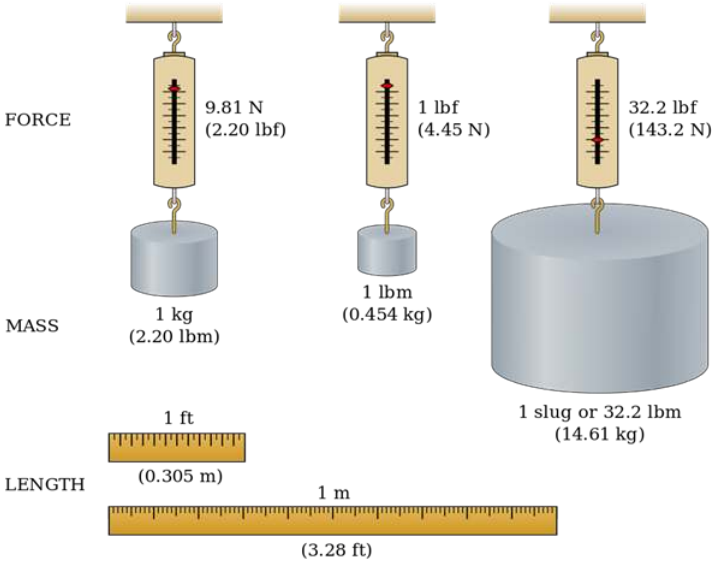


Figure **1.5.4**: Measurement is a combination of a number and a unit. Source: https://www.hiclipart.com/free-trans...lzufr/download

Systems of units

There are different sets of units used in different systems of units. For example, 1.83 meters and 6.00 feet show the same length value but using a unit of 'meter' from the international system of units (SI) and 'foot' from the English system of units. The international system of units (SI) is universally used in scientific work. There are seven base units in SI, as listed in Table 1.

Table 1**:** Base units in the International System of Units (SI).

Measurement	Unit	Abbreviation
Time	second	s
Length	meter	m
Mass	kilogram	kg
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A

Note

The following section is based on the 2019 redefinition of the SI base units: https://en.Wikipedia.org/wiki/2019_redefinition_of_the_SI_base_units#Kilogram, accessed on May 2nd, 2020

Time

Time is the progress of existence and events that occur in succession from the past through the present to the future.

In old times, the time measuring device was the hour sandglass shown in Fig. 1.3.5. The basic unit of time is second (s), a standard unit of time in all the measurements systems. Other units of time are minute (min) which is equal to 60 s, and hour which is equal to 60 min or 3600 s.

Definition: Second

The duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atoms at a temperature of 0 K.



Figure **1.5.5**: German; Half-hour sandglass; Horology. Source: Metropolitan Museum of Art / CC0

Length

Length is a measure of distance, i.e., a numerical measurement of how far apart the objects or points are.

Fig. 1.3.6. illustrated the concept of length. The SI unit of length is a meter (m).

Meter

The meter is defined as the distance that light travels in a vacuum in $\frac{1}{299,792,458}$ of a second.



Figure **1.5.6**: Measure of length. Source: https://www.hiclipart.com/free-trans...nhlxx/download

Mass

The mass of an object is a measure of its inertia.

Inertia is the resistance of any physical object to any change in its velocity. Mass determines the strength of the gravitational attraction of an object to another object -a property commonly used in modern balances for mass measurements, as shown in Fig. 1.3.7. SI unit of mass is the kilogram (kg).

Kilogram

Earlier definition: The mass of one cubic decimeter of water at the melting point of ice.

Current definition: Kilogram (kg) is defined by taking the fixed numerical value of the Planck constant h to be 6.62607015×10^{-34} when expressed in the unit $kg\cdot m^2\cdot s^{-1}$.



Figure **1.5.7**: Laboratory Analytical balance. Source: https://www.hiclipart.com/free-trans...bbigu/download

Temperature

Temperature is a physical property of matter that expresses hotness or coldness, as illustrated in Fig. 1.3.8.

> Temperature is a manifestation of the thermal energy of the matter, which is a source of the flow of energy in the form of heat from a hot object to a cold object when they are in contact with each other.

The SI unit of temperature is Kelvin (K).

Kelvin

Kelvin (K) is defined by taking the fixed numerical value of the Boltzmann constant k to be 1.380649×10^{-23} when expressed in the unit $kg\cdot m^2\cdot s^{-2}\cdot K^{-1}$.

A 0 K, also called absolute zero, is the temperature of a matter at which no energy can be removed as heat from the matter. The freezing point of water is 273.15 K, and the boiling point of water is 373.15 K.

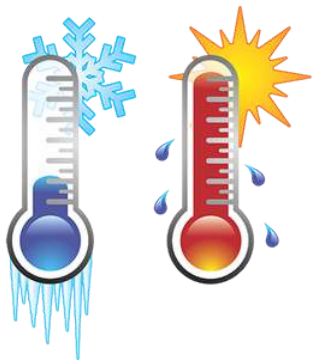


Figure **1.5.8**: An illustration of temperature. Source: https://www.hiclipart.com/free-trans...txxww/download

Amount of substance

In chemistry, the amount of substance (n) measures the number of specified elementary entities. The elementary particles in chemistry are usually atoms in the case of elements and molecules or formula units in the case of compounds. SI unit of the amount of a substance is a mole (mol).

Mole (mol)

Mole is exactly 6.02214076×10^{23} elementary entities.

Fig. 1.3.9 illustrates one mole of aluminum, copper, and carbon. The molar mass is the mass in grams of one mole of that substance, i.e., the mass of 6.02214076×10^{23} atoms or molecules. Usually, the number of particles is shown with four significant figures, i.e., 6.022 x 10^{23} atoms or molecules in one mole of the substance.

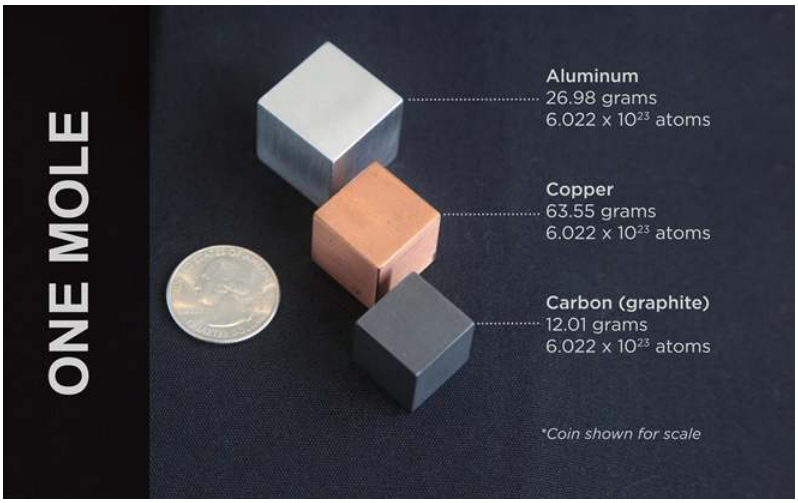


Figure **1.5.9**: Amount in one mole of aluminum, copper, and carbon shown relative to US Quarter coin.

Source: Public information, photo: R. Press/NIST; graphic design: N. Hanacek/NIST

Electric current

> Electric current is the flow rate of electric charge past a point or a region.

It could be the flow of electrons in electric wires or the flow of cations and anions in opposite directions as in electrolytes, as illustrated in Fig. 1.3.10. The SI unit of current is ampere (A).

Definition: Ampere (A)

Ampere (A) is defined by taking charge of an electron (e) to be $1.602176634\times10^{-19}$ coulomb (C), where C is equivalent to ampere-second (A.s).



Figure **1.5.10**: Illustration of the definition and direction of electric current, i.e, the current (I) is the rate of flow charges (Q) per unit time (t). Source: And1mu/ CC-BY-SA-4.0, https://commons.wikimedia.org/wiki/F...ricCurrent.gif

Luminous intensity

> Luminous intensity measures the wavelength-weighted power emitted by a light source in a particular direction per unit solid angle.

The solid angle is measured in steradian (sr), analogous to the radian. The radian is a planar angel that gives the length of the circumference of a circle, and the steradian is a 3D angle, like a cone, that gives an area on the surface of a sphere, as shown in Fig. 1.3.11.

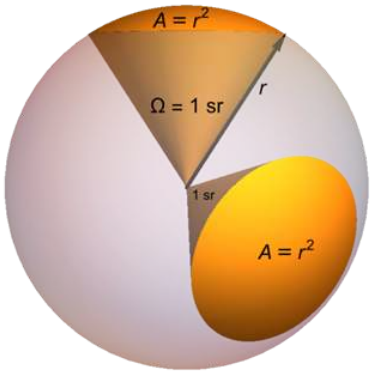


Figure **1.5.11**: A solid angle is a three-dimensional analog of a circular angle that relates a portion of the volume of a sphere to the surface area it subtends. If that area equals the sphere's radius squared, the solid angle is one steradian. This diagram displays two solid angles of one steradian, viewed from different directions. Source: Andy Anderson / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

SI unit of luminous intensity in a given direction is Candela (cd).

Candela (cd)

Candela (cd) is defined by taking the fixed numerical value of the luminous efficacy of monochromatic radiation of frequency 540×10^{12} Hz, K_{cd}, to be 683 $cd\cdot sr\cdot W^{-1}$, or $cd\cdot sr\cdot kg^{-1}\cdot m^{-2}\cdot s^3$, where **W is watt** –a SI unit of power described by $kg.m^2.s^{-3}$.

Prefixes in SI

In several situations, the measured number with the base unit is either too large or too small. For example, a person's height is comfortable to represent in the meter as the height is usually in a 1 m to 2 m range. However, the diameter of the earth, i.e., 12,700,000 m, and the diameter of red blood cells, i.e., 0.000,006 m, are too large and too small, respectively. The unit needs to be revised so that the number with it is easy to read and write.

> Prefixes are used in SI to increase or decrease the base unit by order of tens.

For example, kilo (k) means a thousand times, i.e., 1 km means 1000 m and 1 kg means 1000 g. Similarly, micro (µ) means one-millionth time, i.e., 1 µm is 10^{-6} m, and 1 µg is 10^{-6} g. Table 2 lists commonly used prefixes in SI.

Table 2: Commonly used prefixes in SI (note: m means "meter" in SI units, but as a prefix, it means "mili")

Prefix	Means	Abbreviation
Gega	10^9	G
Mega	10^6	M
Kilo	10^3	k
Deci	10^{-1}	d
Centi	10^{-2}	c
Mili	10^{-3}	m
Micro	10^{-6}	µ
Nano	10^{-9}	n
Pico	10^{-12}	p

A new unit may be defined and used if there is no appropriate prefix available in SI for some specific type of measurement. For example, the diameter of atoms varies in the range of 1 x 10^{-10} m to 5 x 10^{-10} m, where the prefix pico (p, 10^{-12}) is too small, and

the prefix nano (n, 10^{-9}) is large. A new unit called **angstrom** (Å) is defined as 1Å = 10^{-10} m for reporting atomic diameter and inter-atomic distances.

Derived units

> The units in SI other than the seven base units are Derived units obtained by combining the base units.

For example, The SI unit of volume is meter-cube (m^3), equal to the space occupied by a cube of 1m on each edge, as illustrated in Fig. 1.3.12.

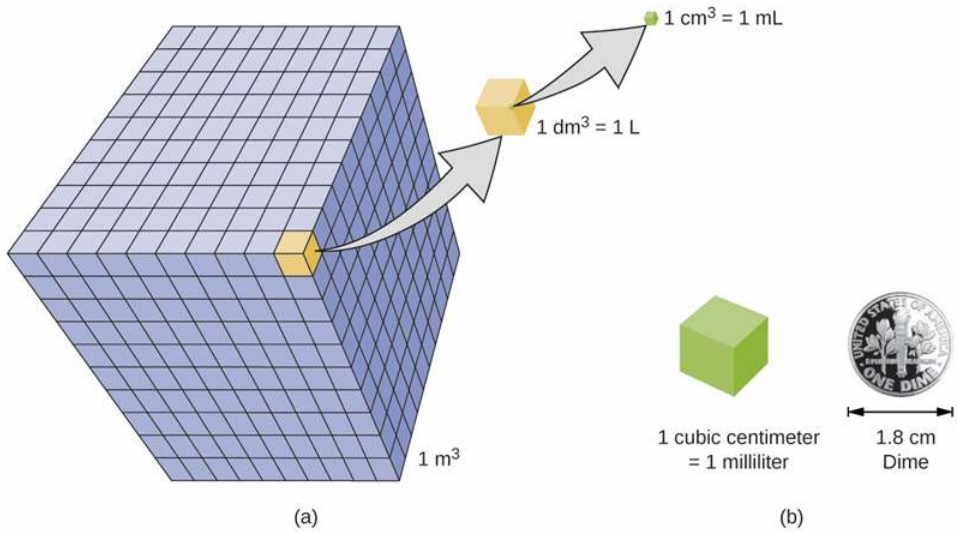


Figure 1.5.12: Relative volume in m^3, dm^3 and cm^3. Diagram of a 10x10x10 cubes. The small cubes represent one decimeter-cube (dm^3); the big cube represents one meter-cube (1 m^3). The purpose is to show that even though there is 10 dm in 1 m, there are 1000 dm^3 in 1 m^3. More generally, it shows that the conversion factor between units of volume is the cube of the conversion factor between corresponding length units. Source: Download for free at https://openstax.org/details/books/chemistry

Usually, the volume is reported in decimeter-cube (dm^3), commonly known as liter (L). One liter is a volume occupied by a cube that is one dm on each edge. Another commonly used unit of volume is the centimeter-cube (cm^3), which is also called cc or mL. One mL is the volume occupied by a cube that is one cm on each edge. The dm^3 is a thousandth of m^3, and cm^3 is the thousandth of dm^3, i.e., 1000 dm^3 = 1 m^3, and 1000 cm^3 = 1 dm^3, as illustrated in Fig. 1.3.11.

Relationship of SI units with metric and English system of units

SI was developed from the metric system. Some basic units are different, but both systems have much in common, using the same prefixes. The English system of units uses a different set of units except for the common unit of time. Table 3 compares the standard measuring units in the three systems of measurement.

Table 3: Common measurement units in three conventional systems of measurements

Quantity	English unit	Metric unit	SI unit	Relationships
Mass	Pound (lb)	Gram (g)	Kilogram (kg)	1 kg = 2.205 lb 1 kg = 1000 g
Length	Foot (ft)	Meter (m)	Meter (m)	1 m = 3.281 ft
Volume	Quart (qt)	Liter (L)	Cubic meter (m^3)	0.946 L = 1 qt 1 m^3 = 1000 L
Energy	calorie (cal)	calorie (cal)	Joule (J)	4.184 J = 1 cal
Temperature	Degree Fahrenheit (°F)	Degree Celsius (°C)	Kelvin (K)	°F = (1.8 × °C) + 32 K = °C + 273.15

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1.6: 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 **1.6.1**.

Example 1.6.1: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

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

Solution

Solutions to Example 2.2.1

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

Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example **1.6.2** illustrates how to do this.

Example 1.6.2: Expressing Sums and Differences in Scientific Notation

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

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

Solution

Solutions to Example 2.2.2.

	Explanation	Answer
a	Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^2) + (47.3 \times 10^2) =$ $(1.36 + 47.3) \times 10^2 = 48.66 \times 10^2$ or $(0.136 \times 10^3) + (4.73 \times 10^3) =$ $(0.136 + 4.73) \times 10^3) = 4.87 \times 10^3$. Choosing either alternative gives the same answer, reported to two decimal places. In converting 48.66 × 10^2 to scientific notation, n has become more positive by 1 because the value of N has decreased.	4.87 × 1
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.	6.04 × 1

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 **1.6.3**.

Example 1.6.3: 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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CHAPTER OVERVIEW

2: Chemistry and Measurements

2.1: Taking Measurements
2.2: The Basic Units of Measurement
2.3: Measuring Mass, Length, and Volume
2.4: Measurement and Significant Figures
2.5: Significant Figures in Calculations
2.6: Problem Solving and Unit Conversions
2.7: Solving Multi-step Conversion Problems
2.8: Density
2.9: Dosage Calculations

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2.1: TAKING MEASUREMENTS

LEARNING OBJECTIVES

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

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



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

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

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

EXAMPLE 2.1.1

Identify the number and the unit in each quantity.

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

SOLUTION

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

KEY TAKE AWAY

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

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2.2: 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).

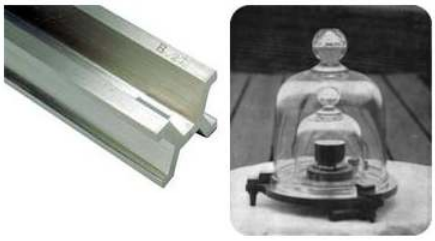


Figure **2.2.1**: Meter standard (left) and Kilogram standard (right).

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.

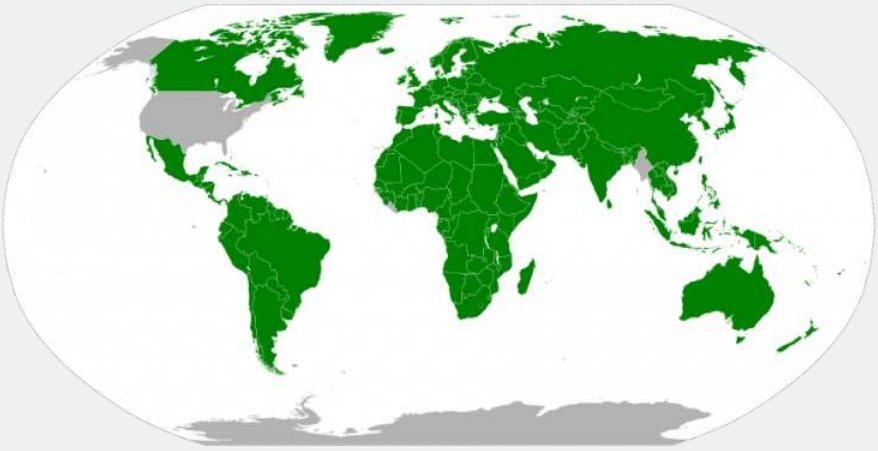


Figure **2.2.1**: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

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

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

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

Example 2.2.1: 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: Measuring Mass, Length, and Volume

Learning Objective

- Describe the units (and abbreviations) that go with various quantities.
- Derive new units by combining numerical prefixes with units.

Mass vs. Weight

One of the many interesting things about travel in outer space is the idea of weightlessness. If something is not fastened down, it will float in mid-air. Early astronauts learned that weightlessness had bad effects on bone structure. If there was no pressure on the legs, those bones would begin to lose mass. Weight provided by gravity is needed to maintain healthy bones. Specially designed equipment is now a part of every space mission so the astronauts can maintain good body fitness.

Mass is a measure of the amount of matter that an object contains. The mass of an object is made in comparison to the standard mass of 1 kilogram. The kilogram was originally defined as the mass of $1\ \text{L}$ of liquid water at 4°C (volume of a liquid changes slightly with temperature). In the laboratory, mass is measured with a balance (see below), which must be calibrated with a standard mass so that its measurements are accurate.



Figure **2.3.1**: An analytical balance makes very sensitive mass measurements in a laboratory, usually in grams.

Other common units of mass are the gram and the milligram. A gram is 1/1000th of a kilogram, meaning that there are $1000\ \text{g}$ in $1\ \text{kg}$. A milligram is 1/1000th of a gram, so there are $1000\ \text{mg}$ in $1\ \text{g}$.

The Difference Between Mass and Weight

The mass of a body is a measure of its inertial property or how much matter it contains. The weight of a body is a measure of the force exerted on it by gravity or the force needed to support it. Gravity on earth gives a body a downward acceleration of about 9.8 m/s^2. In common parlance, weight is often used as a synonym for mass in weights and measures. For instance, the verb “to weigh” means “to determine the mass of” or “to have a mass of.” The incorrect use of weight in place of mass should be phased out, and the term mass used when mass is meant. The SI unit of mass is the kilogram (kg). In science and technology, the weight of a body in a particular reference frame is defined as the force that gives the body an acceleration equal to the local acceleration of free fall in that reference frame. Thus, the SI unit of the quantity weight defined in this way (force) is the newton (N).

Length

Length is the measurement of the extent of something along its greatest dimension. The SI basic unit of length, or linear measure, is the **meter** (m). All measurements of length may be made in meters, though the prefixes listed in various tables will often be more convenient. The width of a room may be expressed as about 5 meters (m), whereas a large distance, such as the distance between New York City and Chicago, is better expressed as 1150 kilometers (km). Very small distances can be expressed in units such as the millimeter or the micrometer. The width of a typical human hair is about 10 micrometers (μm).

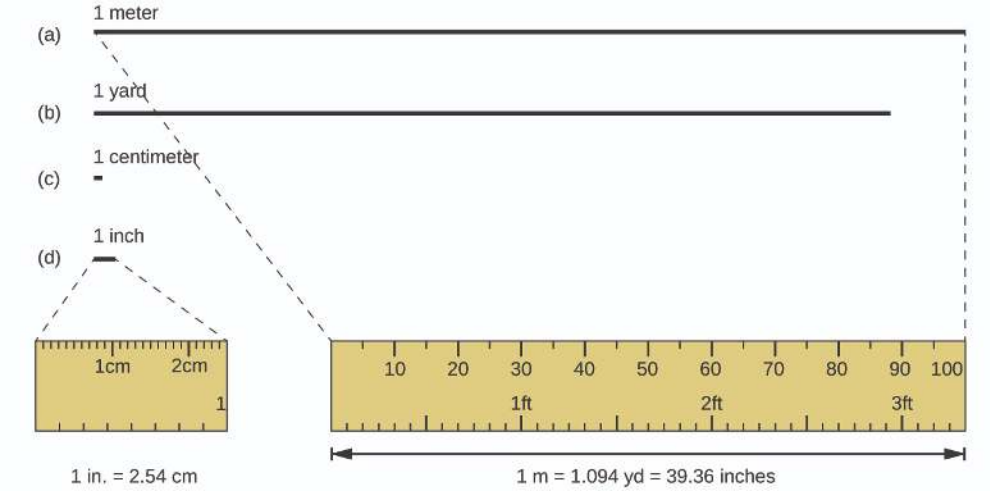


Figure **2.3.2**: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

Volume

In addition to the fundamental units, SI also allows for **derived** units based on a fundamental unit or units. There are many derived units used in science. For example, the derived unit for *area* comes from the idea that area is defined as width times height. Because both width and height are lengths, they both have the fundamental unit of meter, so the unit of area is meter × meter, or meter^2 (m^2). This is sometimes spoken as "square meters." A unit with a prefix can also be used to derive a unit for area, so we can also have cm^2, mm^2, or km^2 as acceptable units for area.

Volume is the amount of space occupied by a sample of matter. The volume of a regular object can be calculated by multiplying its length by its width and its height. Since each of those is a linear measurement, we say that units of volume are derived from units of length. One unit of volume is the cubic meter ($\mathrm{m^3}$), which is the volume occupied by a cube that measures $\mathrm{1\ m}$ on each side. This very large volume is not very convenient for typical use in a chemistry laboratory. A liter (L) is the volume of a cube that measures $\mathrm{10\ cm}$ ($\mathrm{1\ dm}$) on each side. A liter is thus equal to both $\mathrm{1000\ cm^3}$ ($\mathrm{10\ cm \times 10\ cm \times 10\ cm}$) and to $\mathrm{1\ dm^3}$. A smaller unit of volume that is commonly used is the milliliter (mL - note the capital L which is a standard practice). A milliliter is the volume of a cube that measures $\mathrm{1\ cm}$ on each side. Therefore, a milliliter is equal to a cubic centimeter ($\mathrm{cm^3}$). There are $\mathrm{1000\ mL}$ in $\mathrm{1\ L}$, which is the same as saying that there are $\mathrm{1000\ cm^3}$ in $\mathrm{1\ dm^3}$.

Another definition of a liter is one-tenth of a meter cubed. Because one-tenth of a meter is 10 cm, then a liter is equal to 1,000 cm^3 (Figure **2.3.3**). Because 1 L equals 1,000 mL, we conclude that 1 mL equals 1 cm^3; thus, these units are interchangeable.

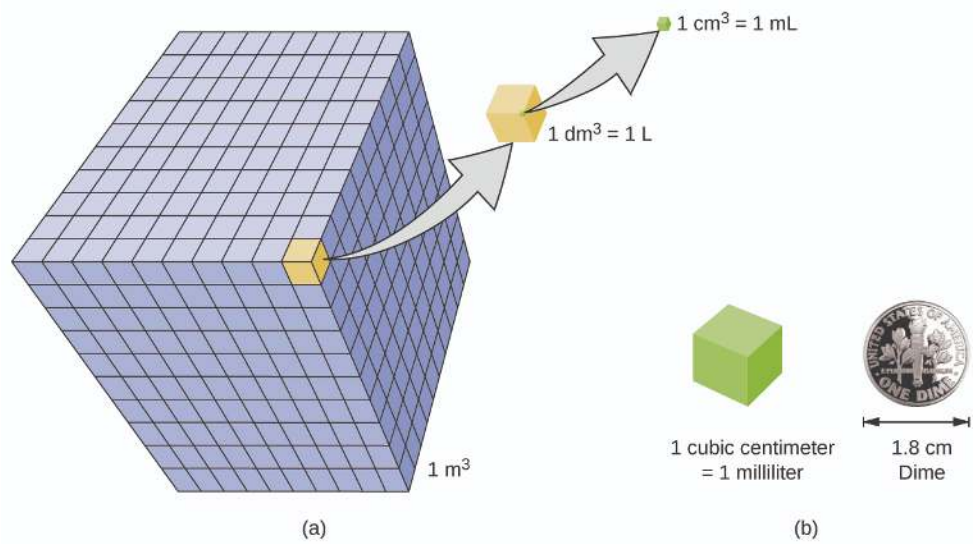


Figure **2.3.3**: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

Units not only are multiplied together but also can be divided. For example, if you are traveling at one meter for every second of time elapsed, your velocity is 1 meter per second, or 1 m/s. The word *per* implies division, so velocity is determined by dividing a distance quantity by a time quantity. Other units for velocity include kilometers per hour (km/h) or even micrometers per nanosecond (μm/ns). Later, we will see other derived units that can be expressed as fractions.

Key Takeaways

- Mass is a measure of the amount of matter that an object contains. Mass is independent of location.
- Weight is a measure of force that is equal to the gravitational pull on an object. Weight depends on location.
- Units can be multiplied and divided to generate new units for quantities like the liter for volume.

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2.4: Measurement and Significant Figures

Learning Objectives

- Identify the number of significant figures in a reported value.
- Apply the concept of significant figures to report a measurement with the proper number of digits.

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used (See Figure **2.4.1**). Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) marked on the meterstick, tell you how many *centimeters* wide the table is. Many metersticks also have markings for millimeters (mm), so we can measure the table to the nearest *millimeter*. The measurement made using millimeters is more precise, it is closer to the actual length of the table. Most metersticks do not have any smaller (or more precise) markings indicated, so you cannot report the measured width of the table any more precise than to the nearest millimeter.

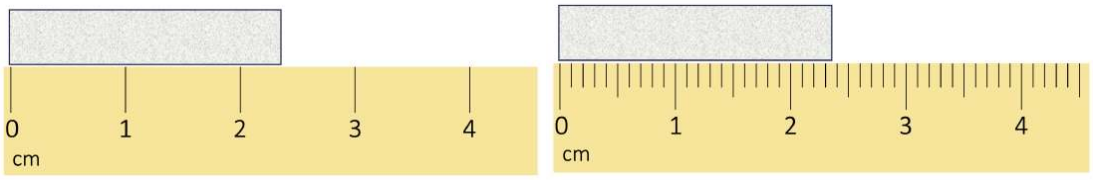


Figure **2.4.1**: Different measuring devices have different degrees of **precision**. The ruler on the left has centimeter markings and the measurement of the box is 2.3 cm. Here, the first digit is *certain*, and the second digit is *estimated*, there are two digits reported for this measurement. The ruler on the right has millimeter markings (1/10 of a centimeter) and the measurement of the box is 2.36 cm. Here, the first two digits are *certain*, and the third digit is *estimated*, there are three digits reported for this measurement. The ruler on the right is more precise than the ruler on the left because more digits are reported. (Figure: Lisa Sharpe Elles)

The concept of **significant figures** takes the limitation of measuring devices into account. The significant figures of a measured quantity are defined as **all** the digits known with *certainty* (those indicated by the markings on the measuring device) *and* the *first* uncertain, or estimated, digit (one digit past the smallest marking on the measuring device). It makes no sense to estimate and report any digits after the first uncertain one, so it is the last significant digit reported in a measurement. Zeros are used when needed to place the significant figures in their correct positions. Thus, zeros are sometimes counted as significant figures but are sometimes only used as placeholders (see the rules for significant figures below for more details).

> *"Sig figs" is a common abbreviation for significant figures.*

Rules for Determination of Significant Figures

Consider the earlier example of measuring the width of a table with a meterstick. If the table is measured and reported as being 1,357 mm wide, the number 1,357 has four significant figures. The 1 (thousands place), the 3 (hundreds place), and the 5 (tens place) are certain; the 7 (ones place) is assumed to have been estimated. It would make no sense to report such a measurement as 1,357.0 (five Sig Figs) or 1,357.00 (six Sig Figs) because that would suggest the measuring device was able to determine the width to the nearest tenth or hundredth of a millimeter, when in fact it shows only tens of millimeters and therefore the ones place was estimated.

On the other hand, if a measurement is reported as 150 mm, the 1 (hundreds) and the 5 (tens) are known to be significant, but how do we know whether the zero is or is not significant? The measuring device could have had marks indicating every 100 mm or marks indicating every 10 mm. How can you determine if the zero is significant (the estimated digit), or if the 5 is significant and the zero a value placeholder?

The **rules** for deciding which digits in a measurement are significant are as follows:

Rule 1: All nonzero digits in a measurement are significant.

- 237 has three significant figures.
- 1.897 has four significant figures.

Rule 2: Zeros that appear between other nonzero digits (i.e., "**middle zeros**") are always significant.

- 20,004 has five significant figures.

- 39.004 has five significant figures.
- 5.02 has three significant figures.

Rule 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.

Rule 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.

- 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.

Rule 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.

It needs to be emphasized that just because a certain digit is not significant does not mean that it is not important or that it can be left out. Though the zero in a measurement of 140 may not be significant, the value cannot simply be reported as 14. An insignificant zero functions as a placeholder for the decimal point. When numbers are written in scientific notation, this becomes more apparent. The measurement 140 can be written as 1.4×10^2, with two significant figures in the coefficient or as 1.40×10^3, with three significant figures. A number less than one, such as 0.000416, can be written in scientific notation as 4.16×10^{-4}, which has 3 significant figures. In some cases, scientific notation is the only way to correctly indicate the correct number of significant figures. In order to report a value of 15,000,00 with four significant figures, it would need to be written as 1.500×10^7.

Exact Quantities

When numbers are known exactly, the significant figure rules do not apply. This occurs when objects are counted rather than measured. For example, a carton of eggs has 12 eggs. The actual value cannot be 11.8 eggs, since we count eggs in whole number quantities. So the 12 is an exact quantity. Exact quantities are considered to have an *infinite number* of significant figures; the importance of this concept will be seen later when we begin looking at how significant figures are dealt with during calculations. Numbers in many conversion factors, especially for simple unit conversions, are also exact quantities and have infinite significant figures. There are exactly 100 centimeters in 1 meter and exactly 60 seconds in 1 minute. Those values are definitions and are not the result of a measurement.

Example 2.4.2

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 explaining how many significant figures are in each number.

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

? Exercise 2.4.2

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 figure.

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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2.5: 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 $207.518\ \text{m}$. 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 2.5.1.

Table 2.5.1: 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 2.5.1

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.

$$\begin{array}{r} 1.2 \\ \underline{4.41} \\ 5.61 \end{array}$$

↑ 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.

$$\begin{array}{r} 77.2 \\ \underline{10.46} \\ 87.66 \end{array}$$

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

Example 2.5.2

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 2.5.2

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



Video **2.5.2**: 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 2.5.3

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

Solution

a.

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

b.

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

c.

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

? Exercise 2.5.3

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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2.6: PROBLEM SOLVING AND UNIT CONVERSIONS

LEARNING OBJECTIVES

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

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

CONVERTING BETWEEN UNITS WITH CONVERSION FACTORS

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

Table 2.6.1: Conversion Factors from SI units to English Units

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

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

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

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

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

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

or

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

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

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

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

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

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

PERFORMING DIMENSIONAL ANALYSIS

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

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

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

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

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

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

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

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

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

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

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

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

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

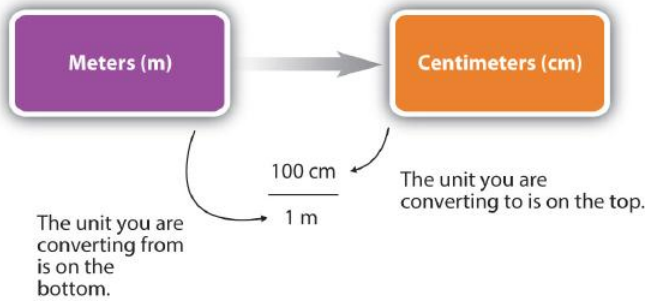


Figure **2.6.1**: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

GENERAL STEPS IN PERFORMING DIMENSIONAL ANALYSIS

1. Identify the "**given**" information in the problem. Look for a number with units to start this problem with.
2. What is the problem asking you to "**find**"? In other words, what unit will your answer have?

3. Use **ratios** and conversion factors to cancel out the units that aren't part of your answer, and leave you with units that are part of your answer.
4. When your units cancel out correctly, you are ready to do the **math**. You are multiplying fractions, so you multiply the top numbers and divide by the bottom numbers in the fractions.

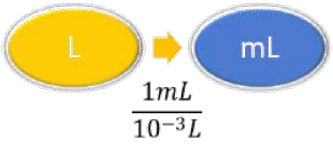
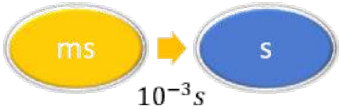
SIGNIFICANT FIGURES IN CONVERSIONS

How do conversion factors affect the determination of significant figures?

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

EXAMPLE 2.6.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

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

EXERCISE 2.6.1

Perform each conversion.

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

Answer a:

$1.01000x10^{-4}s$

Answer b:

$3.208x10^{4}g$

Answer c:

$1.53x10^{2}cg$

SUMMARY

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

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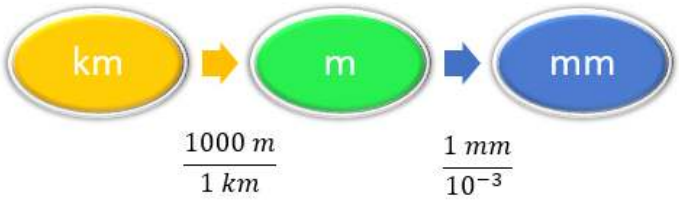
2.7: SOLVING MULTI-STEP CONVERSION PROBLEMS

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 $1\ \text{mm} = 10^{-3}\ \text{m}$.

CONCEPT MAP



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

CALCULATION

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

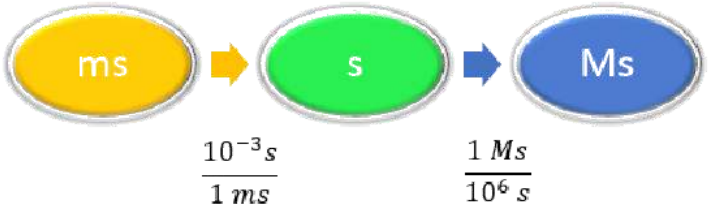
$$= 5.47 \times 10^{7}\ \text{mm}$$

> *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 2.7.1: 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.	 $\frac{10^{-3}s}{1\ ms}$ $\frac{1\ Ms}{10^{6}\ s}$ Convert milliseconds to seconds to microseconds: use conversion factors 0.001 second per millisecond and 1 microsecond per 1 million seconds
Calculate.	$58.2\ \cancel{ms} \times \frac{10^{-3}\cancel{s}}{1\ \cancel{ms}} \times \frac{1\ Ms}{1,000,000\ \cancel{s}} = 0.0000000582\ Ms$ $= 5.82 \times 10^{-8}\ Ms$ Neither conversion factor affects the number of significant figures in the final answer.

EXAMPLE 2.7.2: 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.	 $\frac{24hr}{1\ day}$ $\frac{60min}{1\ hr}$ $\frac{60\ s}{1\ min}$ 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.	$1\ d \times \frac{24\ hr}{1\ d} \times \frac{60\ min}{1\ hr} \times \frac{60\ s}{1\ min} = 86,400\ s$

EXERCISE 2.7.1

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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2.8: 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

$$\rho = \frac{m}{V} \tag{2.8.1}$$

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 **2.8.1**. 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 **2.8.1**: 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 2.8.1: 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 2.8.1:

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

? Exercise 2.8.1

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

Answer a

$0.274\ kg/L$

Answer b

$1.049\ kg/L$

Density as a Conversion Factor

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

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

and

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

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

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

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

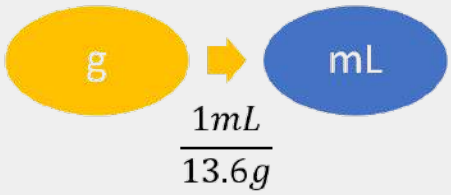
> *Density can be used as a conversion factor between mass and volume.*

✓ Example 2.8.2: Mercury Thermometer Steps for Problem Solving

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

Solution

Solution to Example 2.9.2

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

? Exercise 2.8.2

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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2.9: Dosage Calculations

Learning Objectives

- Calculate drug dosages using conversion factors.

To Your Health: Dosages

A medicine can be more harmful than helpful if it is not taken in the proper dosage. A dosage (or dose) is the specific amount of a medicine that is known to be therapeutic for an ailment in a patient of a certain size. Dosages of the active ingredient in medications are usually described by units of mass, typically grams or milligrams, and generally are equated with a number of capsules or teaspoonfuls to be swallowed or injected. The amount of the active ingredient in a medicine is carefully controlled so that the proper number of pills or spoonfuls contains the proper dose.

Most drugs must be taken in just the right amount. If too little is taken, the desired effects will not occur (or will not occur fast enough for comfort); if too much is taken, there may be potential side effects that are worse than the original ailment. Some drugs are available in multiple dosages. For example, tablets of the medication levothyroxine sodium, a synthetic thyroid hormone for those suffering from decreased thyroid gland function, are available in 11 different doses, ranging from 25 micrograms (µg) to 300 µg. It is a doctor's responsibility to prescribe the correct dosage for a patient, and it is a pharmacist's responsibility to provide the patient with the correct medicine at the dosage prescribed. Thus, proper quantities—which are expressed using numbers and their associated units—are crucial for keeping us healthy.

Effects are dose-dependent

Chemicals are the most common things for which doses are measured, but there are others, such as radiation exposure. For humans, most doses of micronutrients and medications are measured in milligrams (mg), but some are measured in micrograms because of their potency. Nonmedicinal poisons span the measurement scale; some poisons are so dangerous that a single microgram of it could be deadly, whereas other substances take much more. For example, even water is toxic when consumed in large enough quantities.

Dosage (the size of each dose) determines the strength and duration of the health benefits of nutrients, and also of the therapeutic effects of medical treatments. Dosage also determines the severity of adverse effects of treatments and toxins.

Duration of exposure, that is, the period of time over which the dose was received (all at once or gradually) also determines its effects (the body may build tolerance to gradual exposure to a drug, while a large immediate dose could be deadly).

The route by which a dose is exposed to, may affect the outcome, because some medications have different effects depending on whether they are inhaled, ingested, taken transdermally, injected, or inserted.

The dosage, route, concentration, and division over time may all be critical considerations in the administering of drugs, or in responding to exposure to a toxin. In nutrition, the route is usually a given, as nutrients are generally eaten; while dosage and the frequency of ingestion of nutrients are very important variables in preventing disease and promoting overall health.

Calculation of dose

Calculating drug dosages for humans based on the doses used in animal studies can be based on weight (e.g., mg/kg) or surface area (e.g., mg/m2) based on weight2/3.[1]

Drug dosage calculations

Drug dosage calculation is required if the physician's order is different from what is available.

Example 2.9.1

a. A physician ordered 100 mg of Demerol. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?
b. The doctor's order is 1.2 g of Folic Acid. Folic Acid is available as 800 mg per tablet. How many tablets should be taken?

Solution

a. We start with the given, 100 mg. We want to change the unit from *mg* to *tablets*. There are 50 mg in 1 tablet (Remember that *per* tablet means *one* tablet. From this relationship, we can construct the conversion factor. We use the conversion factor that will cancel out the original unit, *mg*, and introduce the unit we are converting to, which is *tablet*.

$$100 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{50 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Hence, the nurse should administer 2 tablets.

b. We start with the given, 1.2 g and we want to change *grams* to number of *tablets*. First, we convert *1.2 g* to *mg* and then convert *mg to tablets*. We need a conversion factor for each step.

$$1.2 \cancel{\text{g}} \times \frac{1{,}000 \cancel{\text{mg}}}{1 \cancel{\text{g}}} \times \frac{1 \text{ tablet}}{800 \cancel{\text{mg}}} = 1.5 \text{ tablets}$$

Hence, 1.5 tablets should be taken.

? Exercise 2.9.1

Calculate each of the following.

a. The physician ordered 20 mg of Valium. Valium is available as 10 mg per tablet. How many tablets should the nurse administer?
b. The doctor's order is 1 g of Calcium. What is on hand is Calcium as 500 mg per tablet. How many tablets should be taken?

Answer a

Start with 20 mg of Valium. For the conversion factor, we know that 10 mg Valium = 1 tablet

$$20 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{10 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Answer b

Start with 1 g (1000 mg) of Calcium. For the conversion factor, we know that 500 mg Calcium = 1 tablet

$$1000 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Drug Dosage Calculation based on Body Weight. Many drugs (especially in children) are dosed according to body weight (mg/kg). These calculations are carried in 3-step conversions. The first step is to convert the body weight from *pounds (lbs)* to *kg*. The second step is to convert *kg* to *mg* (the total *mg dose* calculated based on body weight). And, finally, the *mg dose* is converted to the number of *tablets*. (as in Example 1.8.1).

✓ Example 2.9.2

a. Demerol is ordered 1.5mg/kg for a patient that is 220 lbs. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?
b. A doctor prescribes amoxicillin 30mg/kg to a child weighing 73.5 lbs. Amoxicillin is available as 500 mg tablets. How many tablets should the nurse administer?

Solution

a. We start with the given, 220 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to *total dose (mg)* and then *the mg dose to tablets*. The first conversion factor will cancel out the original unit, *lbs*, and introduce the unit we are converting to, which is *kg*. The second conversion factor will cancel out *kg*, and introduce the unit of the *dose* (usually *mg*) and then *mg* to *tablet*.

$$220 \cancel{\text{lbs}} \times \frac{1 \cancel{\text{kg}}}{2.2 \cancel{\text{lbs}}} \times \frac{1.5 \cancel{\text{mg}}}{1 \cancel{\text{kg}}} \times \frac{1 \text{ tablet}}{50 \cancel{\text{mg}}} = 3 \text{ tablets}$$

Hence, the nurse administers 3 tablets.

b. Start with the given, 73.5 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to total dose (*mg*) and then *mg* to *tablets*. The first conversion factor will cancel out the original unit, *lbs*, and convert to *kg*. The second conversion factor will cancel out *kg*, and convert to the total *mg dose* and the final conversion will cancel *mg* to introduce the final unit, *tablet*.

$$73.5 \cancel{\text{lbs}} \times \frac{1 \cancel{\text{kg}}}{2.2 \cancel{\text{lbs}}} \times \frac{30 \cancel{\text{mg}}}{1 \cancel{\text{kg}}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Hence, the nurse administers 2 tablets.

? Exercise 2.9.2

Calculate each of the following.

a. Vancomycin is ordered 15mg/kg for a patient that is 110 lbs. Vancomycin is available as 250 mg per capsule. How many capsules should the nurse administer? (ans. 3 capsules)
b. A doctor prescribes ampicillin 40mg/kg to a patient weighing 55 lbs. Ampicillin is available as 500 mg tablets. How many tablets should the nurse administer? (ans. 2 tablets)

Answer a

$$110 \cancel{\text{lbs}} \times \frac{1 \cancel{\text{kg}}}{2.2 \cancel{\text{lbs}}} \times \frac{15 \cancel{\text{mg}}}{1 \cancel{\text{kg}}} \times \frac{1 \text{ tablet}}{250 \cancel{\text{mg}}} = 3 \text{ tablets}$$

Answer b

$$55 \cancel{\text{lbs}} \times \frac{1 \cancel{\text{kg}}}{2.2 \cancel{\text{lbs}}} \times \frac{40 \cancel{\text{mg}}}{1 \cancel{\text{kg}}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{mg}}} = 2 \text{ tablets}$$

References

1. The Use of Body Surface Area as a Criterion of Drug Dosage in Cancer Chemotherapy(opens in new window) [cancerres.aacrjournals.org] "The Use of Body Surface Area as a Criterion of Drug Dosage in Cancer Chemotherapy" D Pinkel. Cancer Research 1958

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1.8: Dosage Calculations

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CHAPTER OVERVIEW

3: Matter and Energy

3.1: What is Matter?
3.2: Classifying Matter According to Its Composition
3.3: Classifying Matter According to Its State—Solid, Liquid, and Gas
3.4: Differences in Matter- Physical and Chemical Properties
3.5: Changes in Matter - Physical and Chemical Changes
3.6: Chemical Reactions - Examples of Chemical Change
3.7: Temperature - Random Motion of Molecules and Atoms
3.8: States of Matter and Their Changes

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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".

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3.2: 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 **3.2.1**). 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.

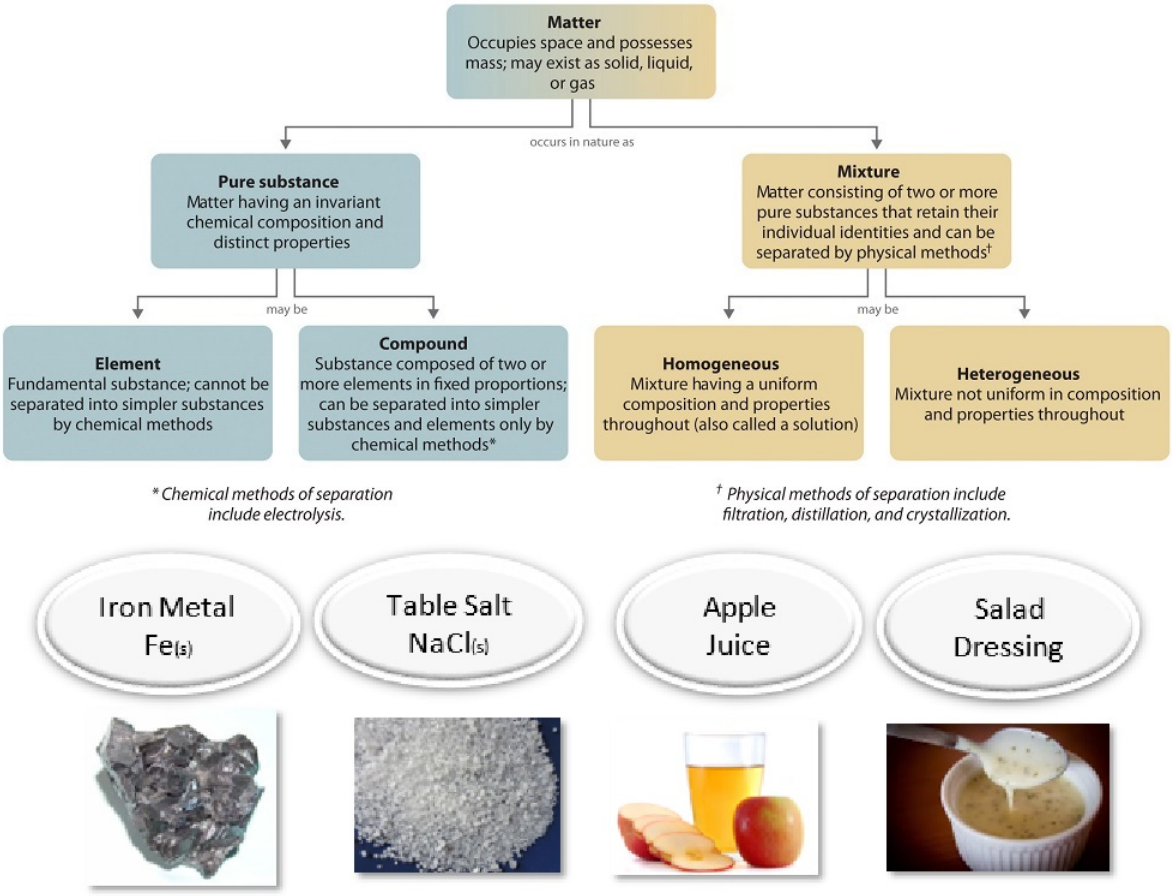


Figure **3.2.1**: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

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 3.2.1

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 3.2.1

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 3.2.2

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 3.2.2

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

Learning Objectives

- To describe the solid, liquid and gas phases.

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

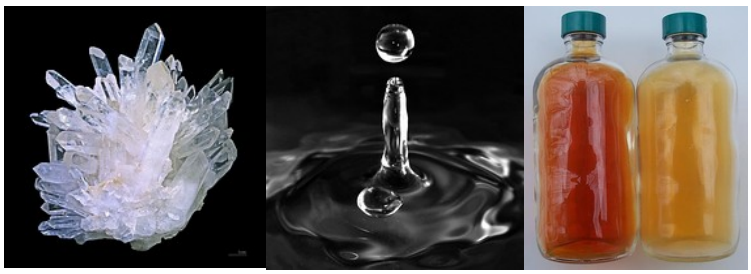


Figure **3.3.1**: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

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

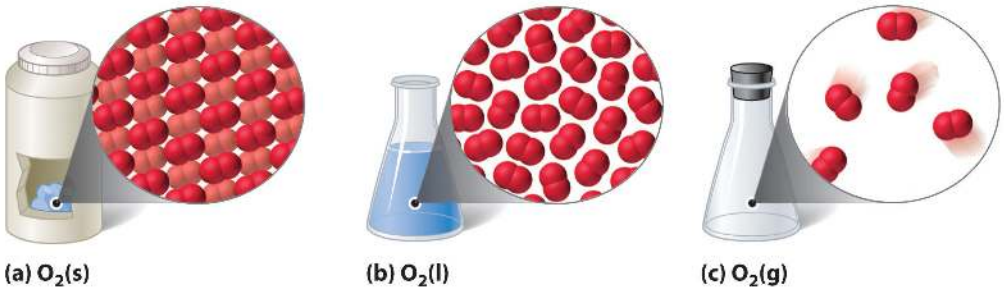
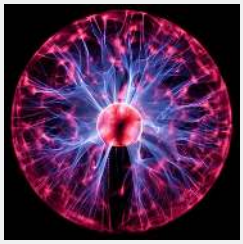


Figure **3.3.2**: A Representation of the Solid, Liquid, and Gas States. (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous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

Plasma: A Fourth State of Matter

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



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

Solids

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

Solids are defined by the following characteristics:

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

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

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

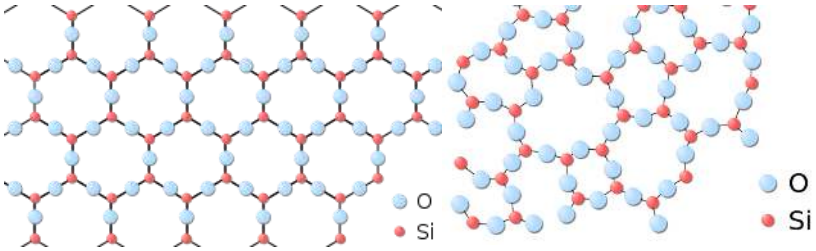


Figure **3.3.3**: (left) The periodic crystalline lattice structure of quartz SiO_2 in two-dimensions. (right) The random network structure of glassy SiO_2 in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view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

Liquids

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

Liquids have the following characteristics:

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

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



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

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

Gases

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

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

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

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

Example 3.3.1

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

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

Solution

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

Exercise 3.3.1

What state or states of matter does each statement describe?

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

Answer a:

solid

Answer b:

gas

Answer c:

solid

Summary

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

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3.4: 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, $\mathbf{CH_4}$, and two molecules of oxygen, $\mathbf{O_2}$; on the right are two molecules of water, $\mathbf{H_2O}$, and one molecule of carbon dioxide, $\mathbf{CO_2}$. 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: $\mathbf{H_2O}\,(l) \rightarrow \mathbf{H_2O}\,(g)$

b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $Fe + O_2 \rightarrow Fe_2O_3$
c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

? Exercise 3.5.1

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.

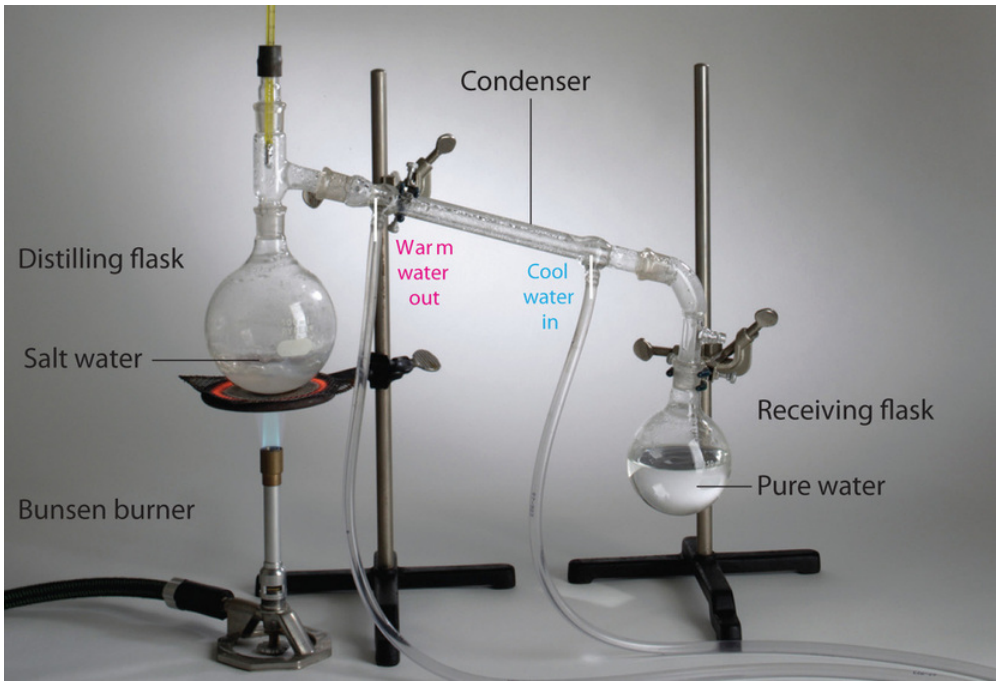


Figure **3.5.3***: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in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

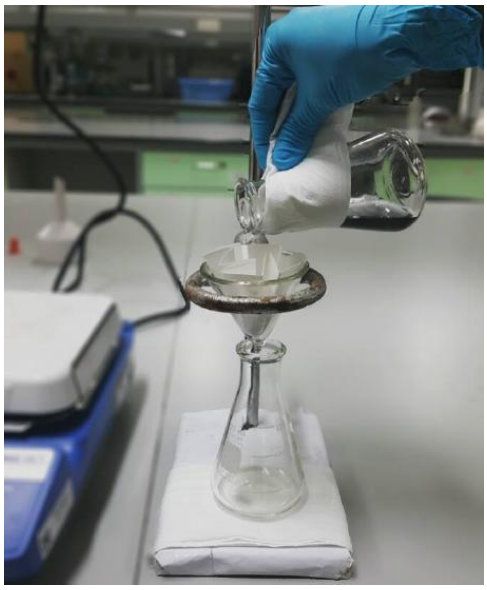


Figure **3.5.4***: Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

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.

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3.6: Chemical Reactions - Examples of Chemical Change

Chemical reactions are the processes by which chemicals interact to form new chemicals with different compositions. Simply stated, a chemical reaction is the process where reactants are transformed into products. How chemicals react is dictated by the chemical properties of the element or compound- the ways in which a compound or element undergoes changes in composition.

Chemical reactions are constantly occurring in the world around us; everything from the rusting of an iron fence to the metabolic pathways of a human cell are all examples of chemical reactions. Chemistry is an attempt to classify and better understand these reactions. One key reaction in modern civilization is combustion



Figure **3.6.1**: An ignited lighter showing the combustion of butane. (Public Domain; Kimmo Palosaari via Wikipedia)

A chemical reaction is typically represented by a **chemical equation**, which represents the change from reactants to products. The left hand side of the equation represents the **reactants**, while the right hand side represents the **products**. A typical chemical reaction is written with stoichiometric coefficients, which show the relative amounts of products and reactants involved in the reaction. Each compound is followed by a parenthetical note of the compound's physical state: (l) for liquid, (s) for solid, (g) for gas. The symbol (aq) is also commonly used in order to represent an aqueous solution, in which compounds are dissolved in water.

Butane is a gas at room temperature and atmospheric pressure and is highly flammable, colorless, easily liquefied gas (under light pressure). Butane can be used for gasoline blending, as a fuel gas, fragrance extraction solvent, either alone or in a mixture with propane, and as a feedstock for the manufacture of ethylene and butadiene, a key ingredient of synthetic rubber. The chemical formula of butane if $\mathbf{C_4H_{10}}$. When oxygen is plentiful, butane burns to form carbon dioxide and water vapor as observed in modern lighters (Figure **3.6.1**).

This reaction in words is:

$$\textbf{butane} + \textbf{oxygen} \rightarrow \textbf{carbon dioxide} + \textbf{water} \tag{3.6.1}$$

and the corresponding chemical equation for this reaction is:

$$2\,C_4H_{10}\,(g) + 13\,O_2\,(g) \longrightarrow 8\,CO_2\,(g) + 10\,H_2O\,(g) \tag{3.6.2}$$

In the above chemical equation, $\mathbf{C_4H_{10}}$ and $\mathbf{O_2}$ are the **reactants** that reacted to form the **products**: $\mathbf{CO_2}$ and $\mathbf{H_2O}$,

Writing Chemical Equations

To write an accurate chemical equation, two things must occur:

1. Each product and reactant must be written using its chemical formula
2. Coefficients are used in front of the chemical formulas to reflect the ratio species (discussed further in a later chapter)
3. Adding the phase of each chemical in parentheses (although this is often dropped for convenience)

Key Takeaways

- Chemical reactions are written to represent chemical changes.
- Chemical formulas are used to represent the reactants (starting substance) and the products (the new substances).

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3.7: Temperature - Random Motion of Molecules and Atoms

Learning Objectives

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

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



Figure **3.7.1**: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

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



Figure **3.7.2**: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right).

The Fahrenheit Scale

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

The Celsius Scale

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

The Kelvin Scale

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

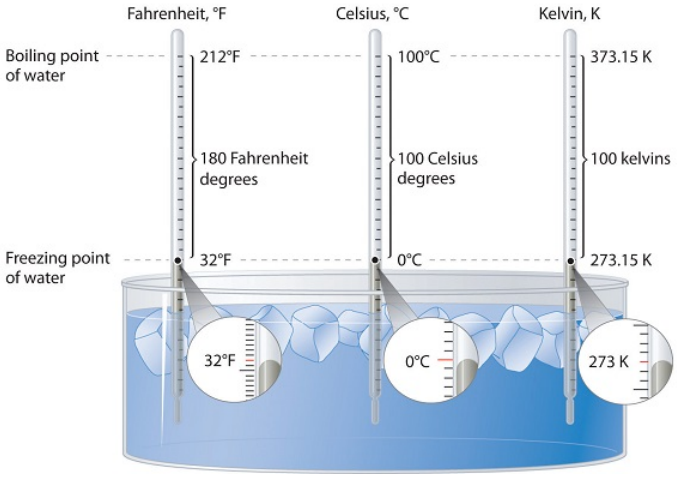


Figure **3.7.1**: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

Converting Between Scales

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

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

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

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

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

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

Example 3.7.1: Temperature Conversions

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

Solution

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

$$°C = \frac{(103.5°F - 32)}{1.8} \tag{3.7.1}$$

$$= 39.7\,°C \tag{3.7.2}$$

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

$$K = 39.7\,°C + 273.15 \quad (3.7.3)$$
$$= 312.9\,K \quad (3.7.4)$$

? Exercise 3.7.1

Convert each temperature to °C and °F.

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

Answer (a)

5527 K, 9980 °F

Answer (b)

2807 K, 5084 °F

Answer (c)

-195.79 K, -320.42 °F

Summary

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

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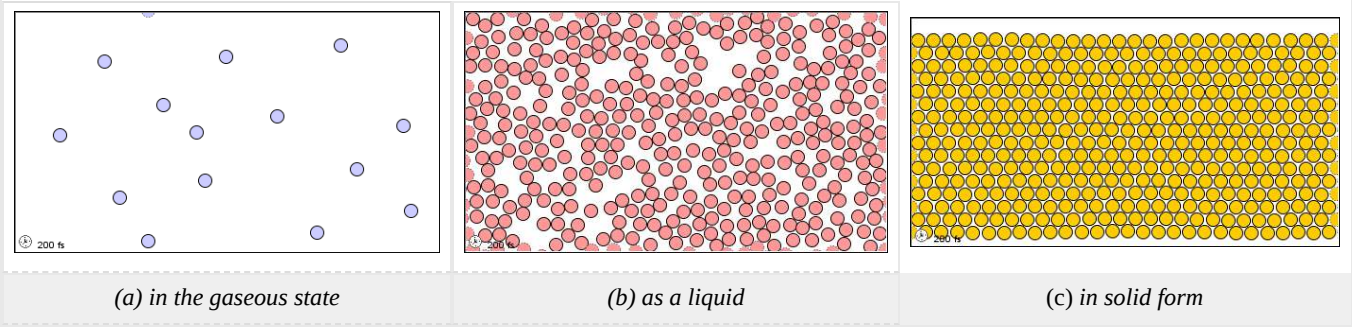
3.8: States of Matter and Their Changes

Learning Objectives

- Review the states of matter and their properties
- Describe how change in temperature will affect the state of matter.

Previously, you were introduced to the three states, also called phases, of matter; solid, liquid, and gas. A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure **3.8.1**).

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the attractive forces between molecules, called *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces draw the particles together. A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.



(a) in the gaseous state | *(b) as a liquid* | (c) *in solid form*

Figure **3.8.1**: Molecular level picture of gases, liquids and solids.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These **changes of state** are often called phase changes. The six most common phase changes are shown in Figure **3.8.2**.

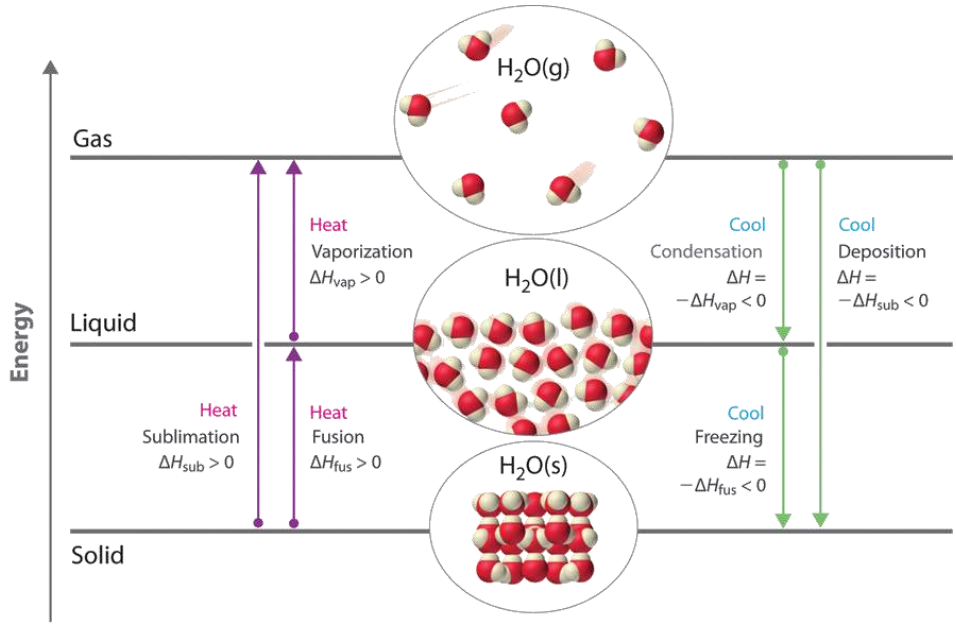


Figure **3.8.2**: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the enthalpy, ΔH, of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; the ΔH is positive (endothermic). Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; the ΔH is negative (exothermic). The energy change associated with each common phase change is shown in Figure **3.8.2**.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The molar **enthalpy of fusion** (ΔH_{fus}), is the energy required to convert a solid to a liquid, a process known as fusion (or melting). As noted above, the process of melting requires energy and therefore, the (ΔH_{fus}) is positive. The reverse process of freezing would release energy making the (ΔH_{fus}) negative. The molar **enthalpy of vaporization** (ΔH_{vap}), is the energy required to convert a liquid to a gas, known as vaporization. Melting points, enthalpies of fusion, boiling points, and enthalpies of vaporization for selected compounds are listed in Table **3.8.1**.

Table **3.8.1**: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

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CHAPTER OVERVIEW

4: Atoms and Elements

4.1: The Elements
4.2: The Periodic Table
4.3: Indivisible - The Atomic Theory
4.4: The Nuclear Atom
4.5: The Properties of Protons, Neutrons, and Electrons
4.6: Elements- Defined by Their Number of Protons
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4.8: Atomic Mass - The Average Mass of an Element’s Atoms
4.9: Electromagnetic Spectrum
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4.1: 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 **4.1.1** shows some of the chemical elements.



Figure **4.1.1**: 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 **4.1.1**: 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 **4.1.1** lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table **4.1.2** lists the relative abundances of elements in the human body. If you compare Table **4.1.1** and Table **4.1.2**, 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 **4.1.1**; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table **4.1.2**: 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, 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 **4.1.3** lists the names and symbols of some of the most familiar elements.

Table **4.1.3**: 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
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 4.1.1

Write the chemical symbol for each element without consulting Table **4.1.3** "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 4.1.1

Write the chemical symbol for each element without consulting Table 4.1.3.

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 4.1.2

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 4.1.2

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.

2.1: The Elements

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4.2: 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 the known elements on the basis of their chemical properties. A modern version is shown in Figure **4.2.1**. 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.

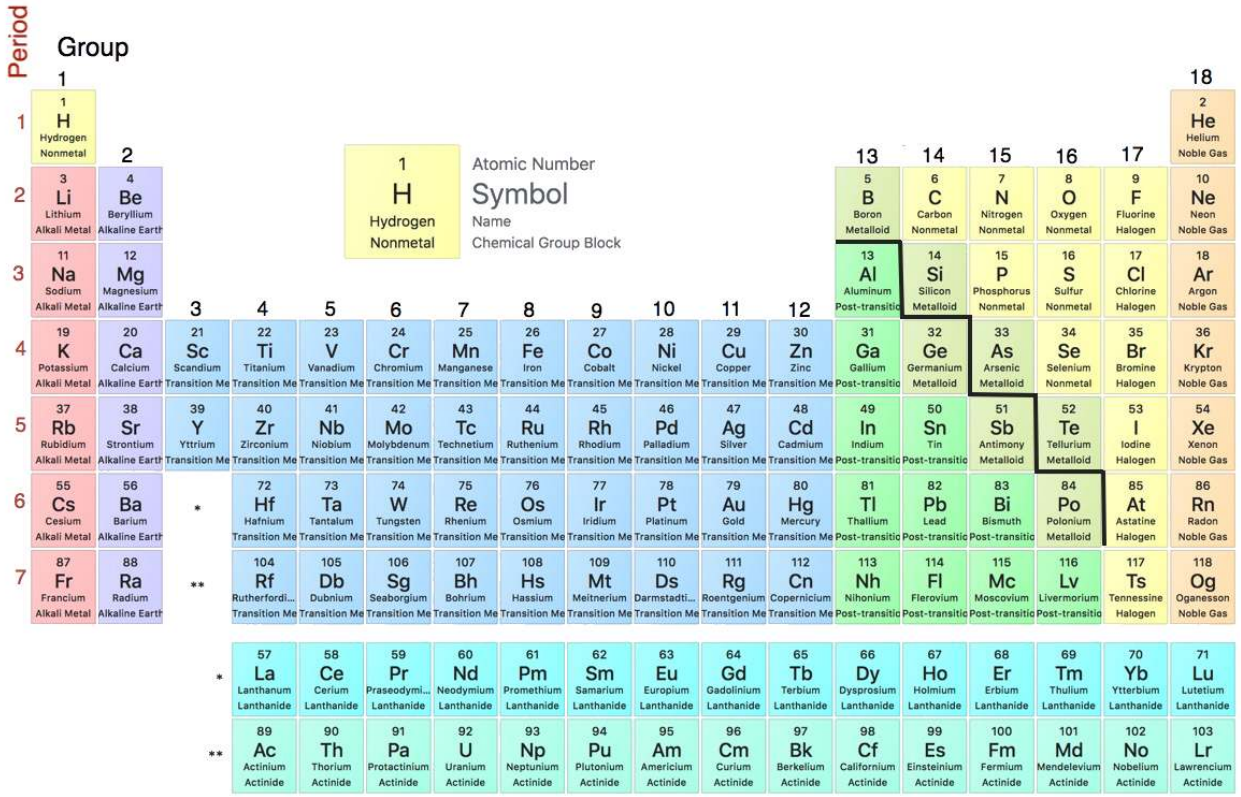


Figure **4.2.1**: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares). An interactive Periodic table can be found here.

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).

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.

Metals, Nonmetals, and Metalloids

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 semimetal, as shown in Figure **4.2.2**. 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 **4.2.2**, **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 **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

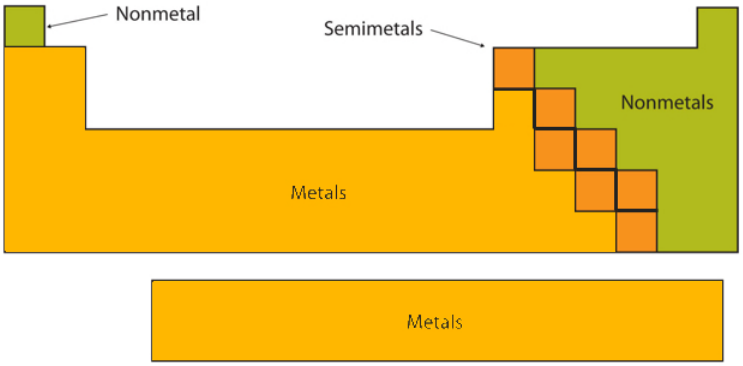


Figure **4.2.2**: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

✔ Example 4.2.1

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. The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure **4.2.2**, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.
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 4.2.1

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

Answer

metal

Representative, Transition, and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure **4.2.3**. The first two columns on the left (groups 1 and 2) and the last six columns on the right (groups 13-19) are called the **main group** or **representative** elements. The ten-column block between these columns (groups 3-12) 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.

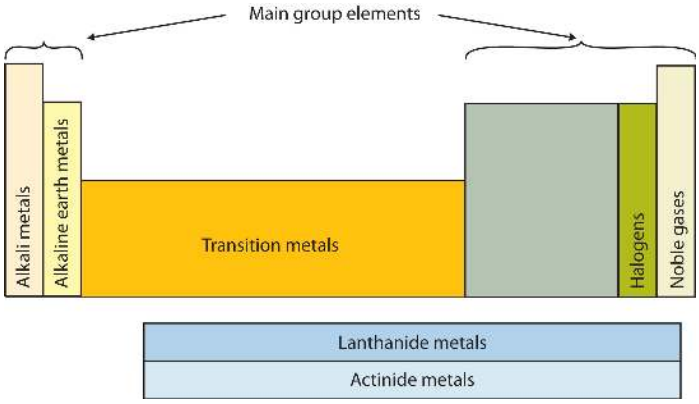


Figure **4.2.3**: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The most abundant non-main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal and the chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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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.

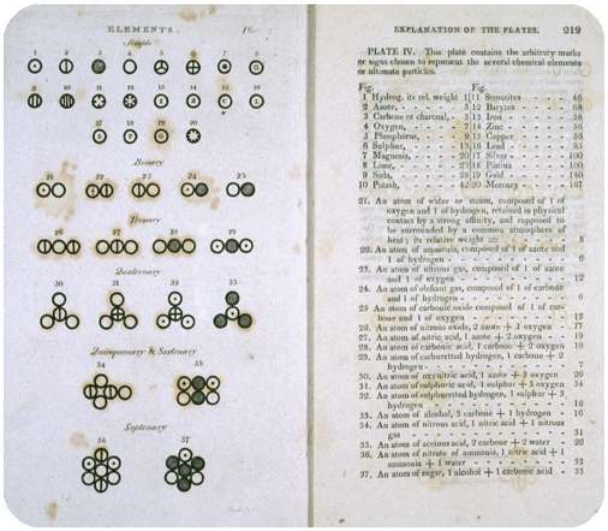
The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **4.3.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual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

EXPLANATION OF THE PLATES. 219

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

Figure **4.3.2**: 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.

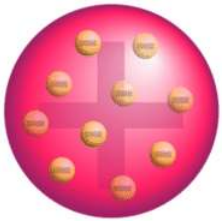


Figure 4.4.2: The "plum pudding" model.

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.

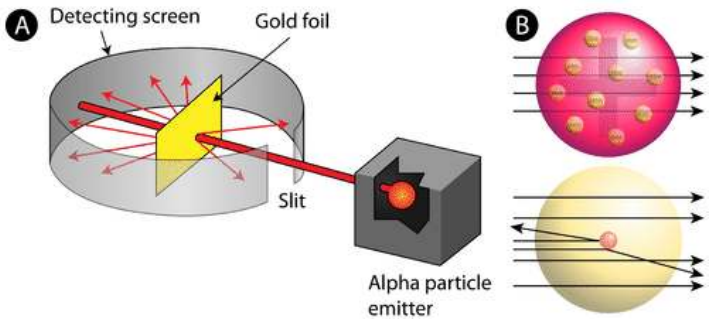


Figure **4.4.3**: (A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding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

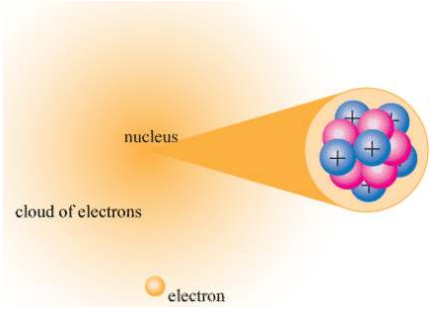


Figure **4.4.4**: The nuclear atom.

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: 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 4.5.1: 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 4.5.1: Properties of Subatomic Particles

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

Table 4.5.1 gives the properties and locations of electrons, protons, and neutrons. The third column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (amu)** is defined as one-twelfth 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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4.6: 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 **4.6.1**: 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 **4.6.1**). 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 **4.6.1**: 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 **4.6.1**). 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 **4.6.1**).

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

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

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

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

Example 4.5.1

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

Solution

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

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

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

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

A **chemical symbol** is a one- or two-letter designation of an element. Some examples of chemical symbols are **O** for oxygen, **Zn** for zinc, and **Fe** for iron. The first letter of a symbol is always capitalized. If the symbol contains two letters, the second letter is lower case. The majority of elements have symbols that are based on their English names. However, some of the elements that have been known since ancient times have maintained symbols that are based on their Latin names, as shown in Table **4.6.2**.

Table **4.6.2**: *Symbols and Latin Names for Elements*

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

Summary

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

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4.7: 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 **4.7.1**. 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.

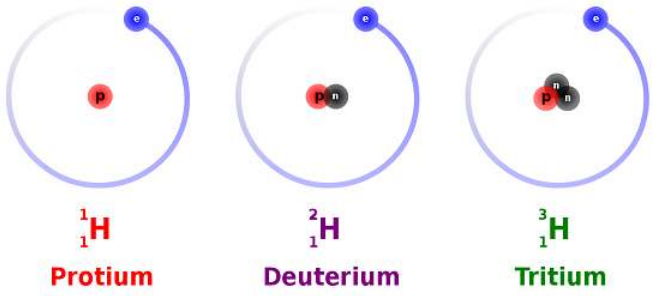


Figure **4.7.1**: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

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 4.7.1: 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.

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

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

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

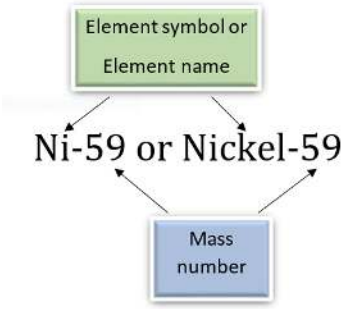
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

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

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

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 4.7.2: Potassium-40

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

Solution

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

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

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

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

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

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

Example 4.7.3: 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 4.7.3

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

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

Answer a:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 neutrons

Answer c:

20 protons, 20 electrons, 25 neutrons

Answer d:

38 protons, 38 electrons, 52 neutrons

Summary

- The number of protons is always the same in atoms of the same element.
- The number of neutrons can be different, even in atoms of the same element.
- Atoms of the same element that contain the same number of protons, but different numbers of neutrons, are known as **isotopes**.
- Isotopes of any given element all contain the same number of protons, so they have the same atomic number (for example, the atomic number of helium is always 2).
- Isotopes of a given element contain different numbers of neutrons, therefore, different isotopes have different mass numbers.

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4.8: 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 4.8.1: 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 4.8.2: Neon Isotopes

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of $19.99\ \text{amu}$. Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of $20.99\ \text{amu}$. The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of $21.99\ \text{amu}$. What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots$$

- Isotope 1: $\%_1 = 0.9092$ (write all percentages as decimals), $\text{mass}_1 = 19.99$

- Isotope 2: $\%_2 = 0.003$, $\text{mass}_2 = 20.99$
- Isotope 3: $\%_3 = 0.0885$, $\text{mass}_3 = 21.99$

Substitute these into the equation, and we get:

$$\text{Atomic mass} = (0.9092)(19.99) + (0.003)(20.99) + (0.0885)(21.99)$$

$$\text{Atomic mass} = 20.17\ \text{amu}$$

The mass of an average neon atom is $20.17\ \text{amu}$

The periodic table gives the atomic mass of each element. The atomic mass is a number that usually appears below the element's symbol in each square. Notice that the atomic mass of boron (symbol **B**) is 10.8, which is what we calculated in Example **4.8.1**, and the atomic mass of neon (symbol **Ne**) is 20.8, which is what we calculated in Example **4.8.2**. 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 4.8.1

Chlorine has two naturally occurring isotopes. In a sample of chlorine, 75.77% of the atoms are Cl-35, with a mass of $34.97\ \text{amu}$. Another 24.23% of the atoms are Cl-37, with a mass of $36.97\ \text{amu}$. What is the atomic mass of chlorine?

Answer

35.45 amu

Summary

- An element's atomic mass is the weighted average of the masses of the isotopes of an element
- An element's atomic mass can be calculated provided the relative abundance of the element's naturally occurring isotopes and the masses of those isotopes are known.
- The periodic table is a convenient way to summarize information about the different elements. In addition to the element's symbol, most periodic tables will also contain the element's atomic number and the element's atomic mass.

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4.9: Electromagnetic Spectrum



Figure 4.9.1 (Credit: Jon Sullivan / pdphoto.org; Source: http://commons.wikimedia.org/wiki/File:Beach_3_bg_121402-1-.jpg(opens in new window); License: Public Domain)

What are waves?

Waves can come in many sizes. Here we see a large wave crashing on the beach. Other waves can be very small and regular. We normally think of waves as being made of water, but there are forms of energy that take on the characteristics of waves. The idea of a wave has played a major role in our understanding of how the atom is put together and why it behaves the way it does.

Properties of Light

The nuclear atomic model proposed by Rutherford was a great improvement over previous models, but was still not complete. It did not fully explain the location and behavior of the electrons in the vast space outside of the nucleus. In fact, it was well known that oppositely charged particles attract one another. Rutherford's model did not explain why the electrons don't simply move toward, and eventually collide with, the nucleus. Experiments in the early twentieth century began to focus on the absorption and emission of light by matter. These studies showed how certain phenomena associated with light reveal insight into the nature of matter, energy, and atomic structure.

Wave Nature of Light

In order to begin to understand the nature of the electron, we first need to look at the properties of light. Prior to 1900, scientists thought light behaved solely as a wave. As we will see later, this began to change as new experiments demonstrated that light also has some of the characteristics of a particle. First, we will examine the wavelike properties of light.

Visible light is one type of **electromagnetic radiation**, which is a form of energy that exhibits wavelike behavior as it moves through space. Other types of electromagnetic radiation include gamma rays, x-rays, ultraviolet light, infrared light, microwaves, and radio waves. The figure below shows the **electromagnetic spectrum**, which is all forms of electromagnetic radiation. Notice that visible light makes up only a very, very small portion of the entire electromagnetic spectrum. All electromagnetic radiation moves through a vacuum at a constant speed of 2.998×10^8 m/s. While the presence of air molecules slows the speed of light by a very small amount, we will use the value of 3.00×10^8 m/s as the speed of light in air.

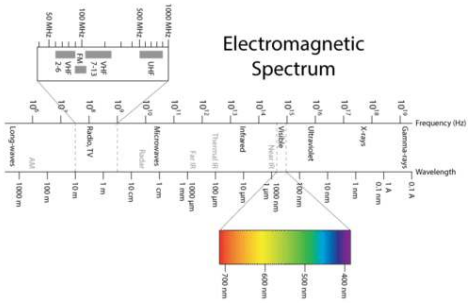


Figure 4.9.2: The electromagnetic spectrum encompasses a very wide range of wavelengths and frequencies. Visible light is only a very small portion of the spectrum with wavelengths from 400-700 nm. (Credit: Zachary Wilson;
Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The figure above shows how the electromagnetic spectrum displays a wide variation in wavelength and frequency. Radio waves have wavelengths of as long as hundreds of meters, while the wavelength of gamma rays are on the order of 10^{-12} m. The corresponding frequencies range from 10^{6} to 10^{21} Hz. Visible light can be split into colors with the use of a prism (see below), yielding the visible spectrum of light. Red light has the longest wavelength and lowest frequency, while violet light has the shortest wavelength and highest frequency. Visible light wavelength ranges from about 400 to 700 nm with frequencies in the range of 10^{14} Hz.

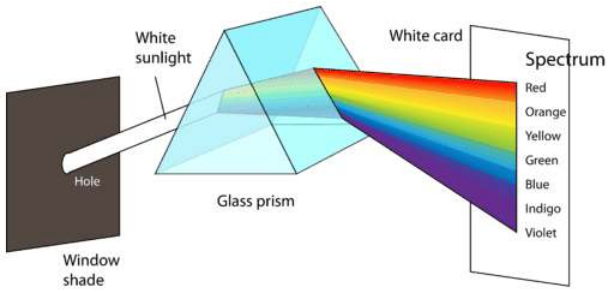


Figure 4.9.3: A small beam of white light is refracted (bent) as it passes through a glass prism. The shorter the wavelength of light, the greater is the refraction, so the light is separated into all of its colors. (Credit: Christopher Auyeung; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))



Summary

- Electromagnetic radiation is a form of energy.
- Visible light has wavelengths from 400-700 nm.
- The speed of light in air is 3.00×10^{8} m/s.

Review

1. What did Rutherford's nuclear atomic model not explain?
2. Prior to 1900, what did scientists believe about the nature of light?
3. What is visible light?
4. What is the range of wavelengths for visible light?

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4.10: Arrangements of Electrons

Learning Objectives

- Describe how electrons are grouped within atoms.

Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space about the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

The modern theory of electron behavior is called quantum mechanics. It makes the following statements about electrons in atoms:

- Electrons in atoms can have only certain specific energies. We say that the energies of the electrons are quantized.
- Electrons are organized according to their energies into sets called **shells** (labeled by the principle quantum number, ***n***). Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.
- Shells are further divided into subsets of electrons called **subshells**. The first shell has only one subshell, the second shell has two subshells, the third shell has three subshells, and so on. The subshells of each shell are labeled, in order, with the letters *s*, *p*, *d*, and *f*. Thus, the first shell has only a single *s* subshell (called **1*s***), the second shell has **2*s*** and **2*p*** subshells, the third shell has **3*s***, **3*p***, and **3*d*** and so forth.

Table **4.10.1**: Shells and Subshells

Shell	Number of Subshells	Names of Subshells
1	1	*1s*
2	2	*2s* and *2p*
3	3	*3s*, *3p* and *3d*
4	4	*4s*, *4p*, *4d* and *4f*

- Different subshells hold a different maximum number of electrons. **Any *s* subshell can hold up to 2 electrons; *p*, 6; *d*, 10; and *f*, 14.**

Table **4.10.2**: Number of Electrons

Subshell	Maximum Number of Electrons
s	2
p	6
d	10
f	14

It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

We use numbers to indicate which shell an electron is in. As shown in Table **4.10.1**, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1}s^{\mathbf{1}}$ to describe the electronic structure of hydrogen. This structure is called an electron configuration. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as “one-ess-one.”

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $\mathbf{1}s^2$ (spoken as “one-ess-two”).

The 1*s* subshell cannot hold 3 electrons (because an *s* subshell can hold a maximum of 2 electrons), so the electron configuration for a lithium atom cannot be $1s^3$. Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell. The second shell has two subshells, *s* and *p*, which fill with electrons in that order. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. Because lithium’s final electron goes into the 2*s* subshell, we write the electron configuration of a lithium atom as $\mathbf{1}s^2\mathbf{2}s^1$**.** The shell diagram for a lithium atom is shown below. The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1*s***, while the outermost shell (**2*s***) has 1 electron.

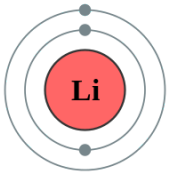


Figure **4.10.1**: Shell diagram of lithium (Li) atom.

The next largest atom, beryllium, has 4 electrons, so its electron configuration is $1s^22s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms start filling the 2*p* subshell. Thus, the electron configurations for the next six atoms are as follows:

- B: $1s^22s^22p^1$
- C: $1s^22s^22p^2$
- N: $1s^22s^22p^3$
- O: $1s^22s^22p^4$
- F: $1s^22s^22p^5$
- Ne: $1s^22s^22p^6$

With neon, the 2*p* subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled *s*, *p*, and *d*. The *d* subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^22s^22p^63s^23p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms. A fourth subshell, the *f* subshell, is needed to complete the electron configurations for all elements. An *f* subshell can hold up to 14 electrons.

Electron filling always starts with **1*s***, the subshell closest to the nucleus. Next is **2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc., shown in the electron shell filling order diagram in Figure **4.10.2**. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

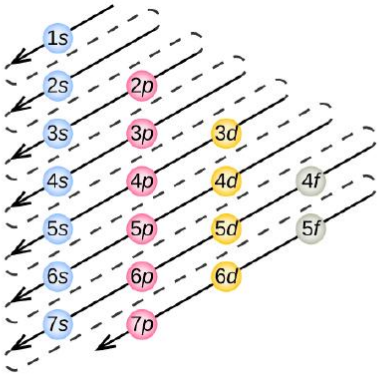


Figure **4.10.2**: The order of electron filling in an atom.

Example 4.10.1: Electronic Configuration of Phosphorus Atoms

Using Figure **4.10.2** as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

Solution

A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3*s* subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

Exercise 4.10.1: Electronic Configuration of Chlorine Atoms

Using Figure **4.10.2** as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

Answer

A neutral chlorine atom has 17 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3*s* subshell, and the remaining 5 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

Since the arrangement of the periodic table is based on the electron configurations, Figure **4.10.3** provides an alternative method for determining the electron configuration. The filling order simply **begins at the top left,** with hydrogen (Z=1) and includes each subshell as you proceed in increasing atomic number (*Z)* order.

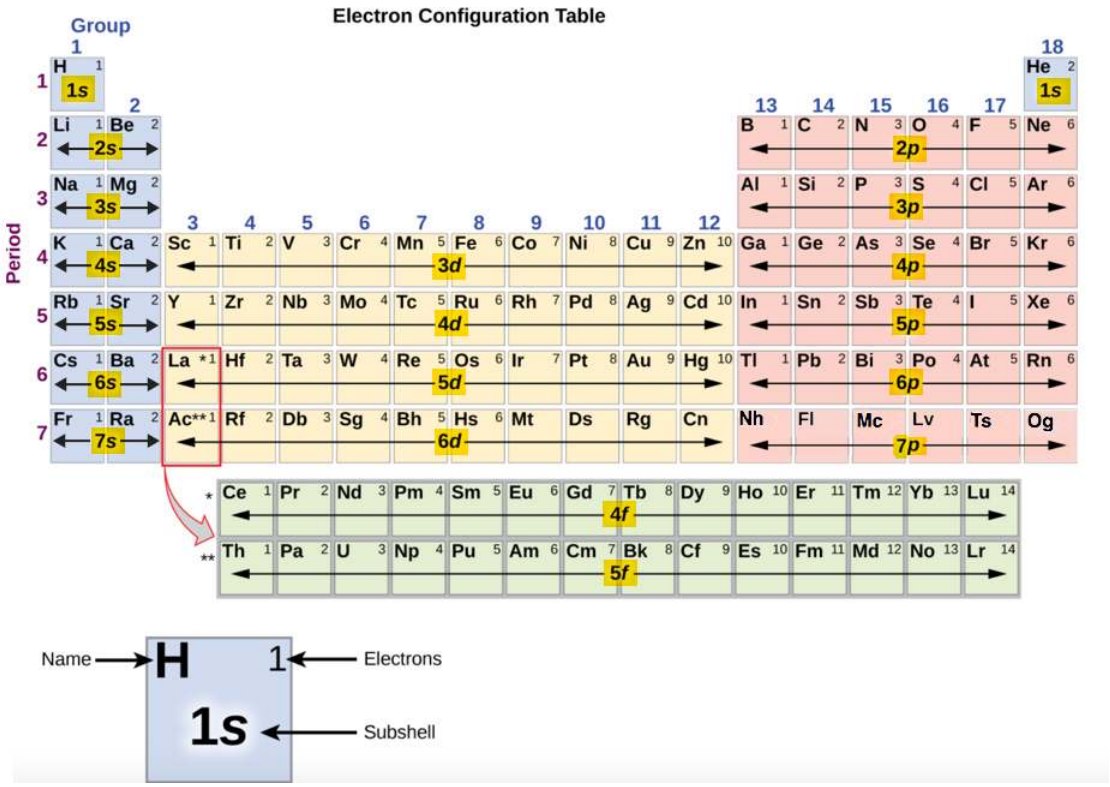


Figure **4.10.3**: This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

For example, the first row (Period 1) contains H and He only, because only two electrons are required to fill the 1s subshell. The second row s-block, contains only two elements, Li and Be, to fill the 2s subshell. This is followed by the second row p-block, containing 6 elements (B through Ne) since six electrons are required to fill the 2p subshell. The third row is similar to the second row elements. Two electrons are needed (Na and Mg) to fill the 3s subshell and six electrons are required (Al through Ar) to complete the 3p subshell. After filling the 3*p* block up to Ar, we see the next subshell will be 4s (K, Ca), followed by the 3*d* subshell, which are filled by ten electrons (Sc through Zn). The 4p subshell is filled next by six electrons (Ga through Kr). As you can see, the periodic table shown in Figure **4.10.3** provides a simple way to remember the order of filling the subshells in determining the electron configuration. The order of filling subshells is the same: **1s, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc.

✔ Example 4.10.2: Aluminum

Using Figure **4.10.3** as your guide, write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

Start at Period 1 of the periodic table, Figure **4.10.3**. Place two electrons in the 1s subshell (**$1s^2$**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**$3s^2$**) and the last one electron in the 3p subshell (**$3p^1$**).

The electron configuration of Aluminum is **$1s^2 2s^2 2p^6 3s^2 3p^1$**

4.10.2 Exercise

Using Figure **4.10.3** as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure **4.10.3**. Place two electrons in the 1s subshell (**$1s^2$**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**$3s^2$**) and the next six electron in the 3p subshell (**$3p^6$**).

Proceed to Period 4. Place the remaining two electrons in the 4s subshell (**$4s^2$).**

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

Valence Electrons

In the study of chemical reactivity, we will find that the electrons in the outermost principal energy level are very important and so they are given a special name. **Valence electrons** are the electrons in the highest occupied principal energy level of an atom.

In the second period elements, the two electrons in the **1*s*** sublevel are called **inner-shell electrons** and are not involved directly in the element's reactivity or in the formation of compounds. Lithium has a single electron in the second principal energy level and so we say that lithium has one valence electron. Beryllium has two valence electrons. How many valence electrons does boron have? You must recognize that the second principal energy level consists of both the **2*s*** and the **2*p*** sublevels and so the answer is three. In fact, the number of valence electrons goes up by one for each step across a period until the last element is reached. Neon, with its configuration ending in **$2s^2 2p^6$**, has eight valence electrons.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** (Figure

\PageIndex4). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

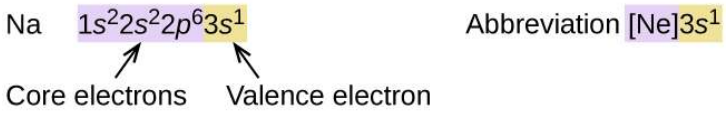


Figure 4.10.4: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

Li : [He] $2s^1$
Na : [Ne] $3s^1$

A chemical reaction results from electron removal, electron addition, or electron sharing of the valence electrons of the different atoms. The path a specific element will take depends on where the electrons are in the atom and how many there are. Thus, it is convenient to separate electrons into two groups. Valence shell electrons (or, more simply, the *valence electrons*) are the electrons in the highest-numbered shell, or valence shell, while core electrons are the electrons in lower-numbered shells. We can see from the electron configuration of a carbon atom—$1s^2 2s^2 2p^2$—that it has 4 valence electrons ($2s^2 2p^2$) and 2 core electrons ($1s^2$). You will see in the next chapters that the chemical properties of elements are determined by the number of valence electrons.

Example 4.10.3

Examine the electron configuration of neutral phosphorus atoms in Example 4.10.1, $1s^2 2s^2 2p^6 3s^2 3p^3$ and write the abbreviated notation.

Solution

Phosphorus has electron configuration, $1s^2 2s^2 2p^6 3s^2 3p^3$.

The highest-numbered shell is the third shell ($3s^2 3p^3$): **2 electrons** in the 3*s* subshell and **3 electrons** in the 3*p* subshell. That gives a total of **5 valence electrons**.

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by [Ne] (see Figure 4.10.3). Abbreviated notation is : [Ne]$3s^2 3p^3$

Exercise 4.10.3

Examine the electron configuration of neutral calcium atom (Exercise 4.10.2), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

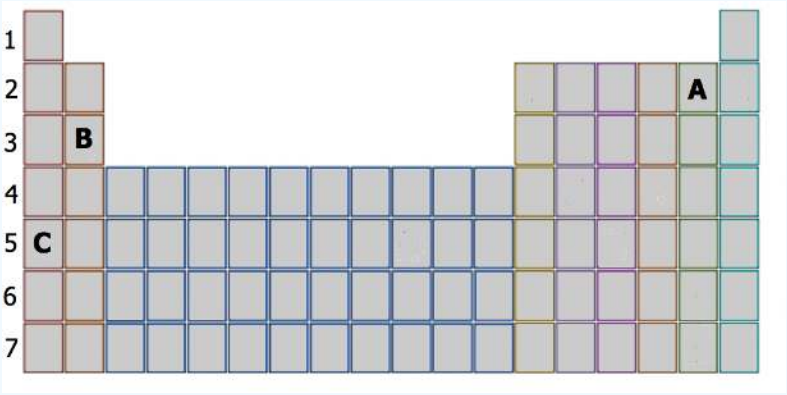
Answer

The highest-numbered shell is the fourth shell $4s^2$, which has **2 electrons** in the *4s* subshell. Hence, Calcium has **2 valence electrons**.

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by [Ar], see Figure 4.10.3. The abbreviated notation is: [Ar]$4s^2$

Example 4.10.4

Based on their respective locations in the periodic table (use Figure **4.10.3**), determine the number of valence electrons and the valence shell configuration of elements A, B and C.



Solution

Element A is located in Period 2, the *5th position* in *2p*-block. Before the electrons are placed in *2p* subshell, the *2s* subshell must be filled first. This means that A has ***two valence electrons*** in 2s (**$2s^2$**) and ***five valence electrons*** in 2p (**$2p^5$**). Answer: **$2s^2 2p^5$.** It has ***2 + 5 = 7*** **valence electrons.**

Element B is located in Period 3, the *2nd position* in *3s*-block. This means that B has ***two valence electrons*** in 3s (**$3s^2$**). Answer: **$3s^2$.**

Element C is located in Period 5, the *1st position* in *5s*-block). This means that there is only **one valence electron** in 5s (**$5s^1$**). Answer: **$5s^1$**.

4.10.4 Exercise

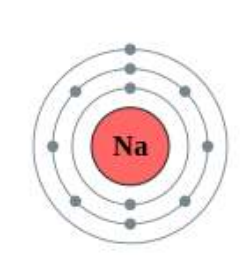
Using the location of Na is the periodic table (Figure **4.10.3**), draw the shell diagram of sodium atom.

Answer

Sodium (Na) is the first element in the 3rd row (Period 3) in the periodic table. This means that the first shell and second shells of Na atom are filled to the maximum number of electrons.

The first shell **(1s)** *is filled with* ***2 electrons***. The second shell (2s and 2p) has a **total of *8 electrons***. And, the third (last) shell has ***1 electron***.

The shell diagram of the Na atom is shown below. The shell nearest the nucleus (first shell) has 2 electrons (2 dots), the second shell has 8 electrons and the last (outermost) shell has 1 electron. (**2.8.1**)



Concept Review Exercises

1. How are electrons organized in atoms?
2. What information does an electron configuration convey?

3. What is the difference between core electrons and valence electrons?

Answers

1. Electrons are organized into shells and subshells around nuclei.
2. The electron configuration states the arrangement of electrons in shells and subshells.
3. Valence electrons are in the highest-numbered shell; all other electrons are core electrons.

Key Takeaway

- Electrons are organized into shells and subshells about the nucleus of an atom.
- The valence electrons determine the reactivity of an atom.

Exercises

2.6: Arrangements of Electrons

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4.11: 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 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.

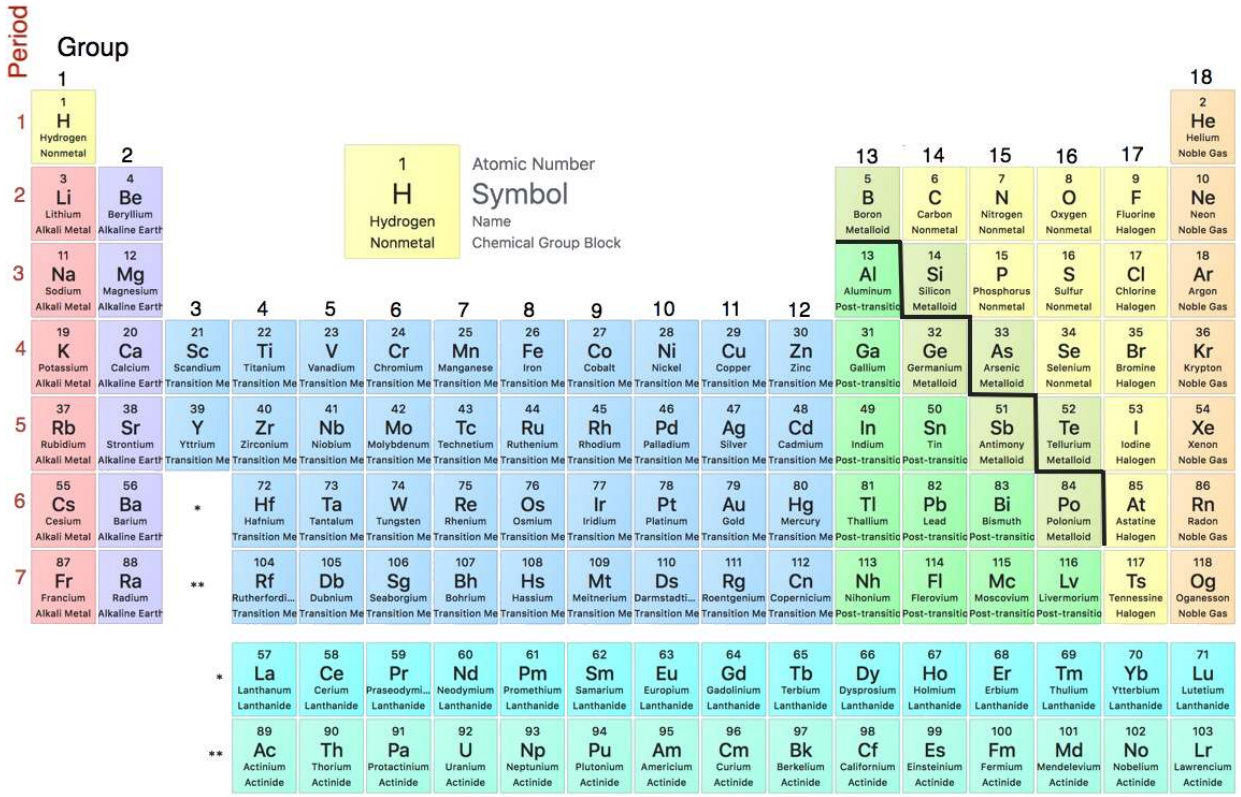


Figure **4.11.1**: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

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).

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.

Metals, Nonmetals and Metalloids

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 semimetal, 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 **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

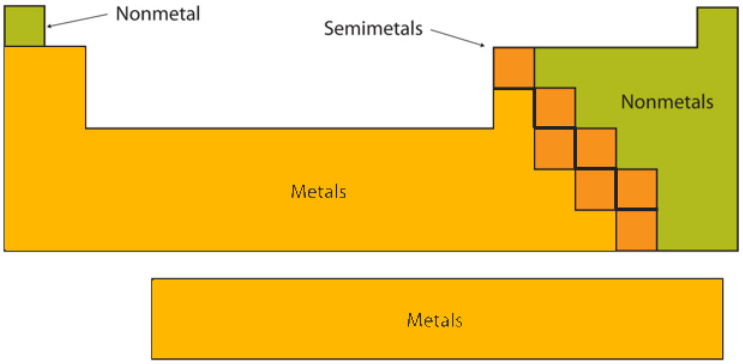


Figure **4.11.2**: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 4.11.1

Based on its position in the periodic table, do you expect selenium (Se) to be a metal, a nonmetal, or a semimetal?

Solution

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.7.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

4.11.1 Exercise

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

Answer

metal

Representative, Transition and Inner-transition

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** or **representative** 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**.

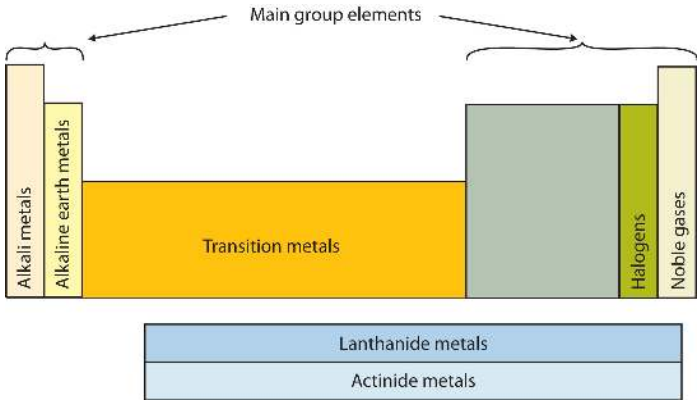


Figure **4.11.3**: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

Alkali metals are the first column. Alkaline earth metals are the second. Halogens are the second to last column. Noble gases are the last column.

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are not listed explicitly in Table 2.1.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

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.

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure **4.11.4**. Starting with the first

period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry.**

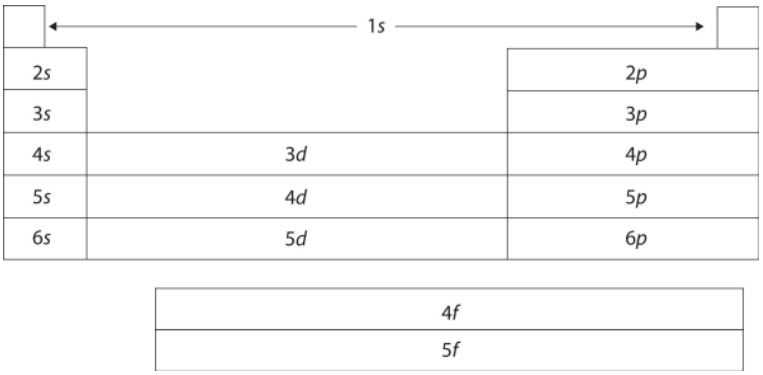


Figure **4.11.4** The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 4.11.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the alkaline earth metals
b. the column of elements headed by carbon

Answer a

The alkaline earth metals are in the second column of the periodic table. This column corresponds to the *s* subshell being filled with 2 electrons. Therefore, the valence shell electron configuration is ns^2.

Answer b

The electron configuration of carbon is $1s^22s^22p^2$. Its valence shell electron configuration is $2s^22p^2$. Every element in the same column should have a similar valence shell electron configuration, which we can represent as ns^2np^2.

Exercise 4.11.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the halogens
b. the column of elements headed by oxygen

Answer a

The halogens are in the 17th column (or Group 7A) of the periodic table. This column corresponds to the *p* subshell being filled with 5 electrons. Therefore, the valence shell electron configuration is ns^2np^5.

Answer b

The column headed by O is the 16th column (or Group 6A). This column corresponds to the *p* subshell being filled with 4 electrons. Therefore, the valence shell electron configuration is ns^2np^4.

Valence Electrons and Group Number

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

Table **4.11.1**. The Group number and the number of valence electrons.

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

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

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

Atomic Radius

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure **4.11.5**). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an $\mathbf{H_2}$ molecule is measured to be $\mathbf{74\ pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = \mathbf{37\ pm}$.

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure **4.11.5**

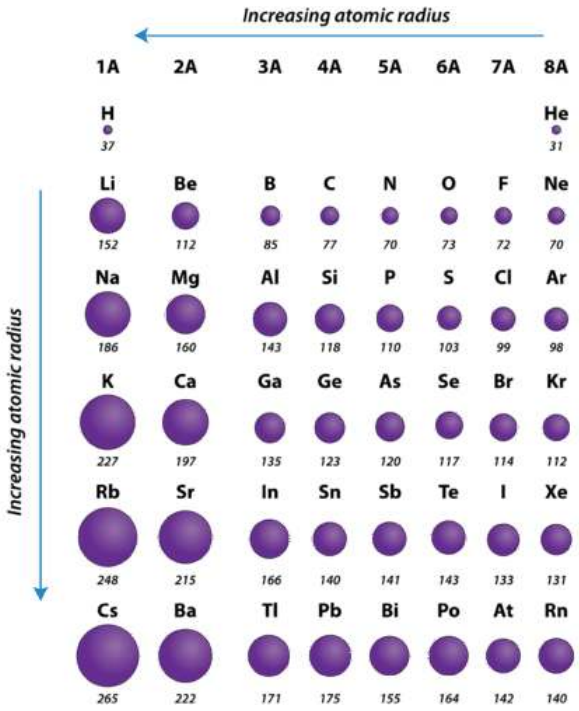


Figure **4.11.5** Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

✔ Example 4.11.2

Using the periodic table (rather than Figure **4.11.5**), which atom is larger?

a. N or Bi
b. Mg or Cl

Answer a

Bi is below N in Group 5A in the periodic table and has electrons in higher-numbered shells, hence we expect that Bi atoms are larger than N atoms.

Answer b

Both Mg and Cl are in period 3 of the periodic table, but Cl lies farther to the right. Therefore we expect Mg atoms to be larger than Cl atoms.

? Exercise 4.11.2

Using the periodic table (rather than Figure **4.11.5**), which atom is larger?

a. Li or F
b. Na or K

Answer a

Li and F are on the same period, but F lies farther to the right. Therefore, we expect Li to be larger than F atoms.

Answer b

K lies below Na in Group 1A, hence has more electron shells, making it larger than Na.

Career Focus: Clinical Chemist

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

Concept Review Exercises

1. How are the elements organized into the periodic table?
2. Looking at the periodic table, where do the following elements appear?
   a. the metals
   b. the nonmetals
   c. the halogens
   d. the transition metals
   e. the noble gases
3. Describe the trends in atomic radii as related to an element's position on the periodic table.

Answers

1. Elements are organized in order of increasing atomic number.
2. a. the left three-quarters of the periodic table (to the left of the zigzag band)
   b. the right quarter of the periodic table (to the right of the zigzag band)
   c. the next-to-last column of the periodic table
   d. the middle section of the periodic table
   e. the last column of the periodic table
3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.
- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic Table. Elements with the same number of valence electrons have similar chemical properties.

2.7: The Periodic Table

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CHAPTER OVERVIEW

5: Ionic and Molecular Compounds

5.1: Ions and Ionic Compounds
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5.14: Physical Properties and Intermolecular Forces

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5.1: Ions and Ionic Compounds

Learning Objectives

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

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

Individual atoms can gain or lose electrons. When they do, they become *monatomic* ions. When atoms gain or lose electrons, they usually gain or lose a characteristic number of electrons and so take on a characteristic overall charge. Table 5.1.1 lists some common ions in terms of how many electrons they lose (making cations) or gain (making anions). There are several things to notice about the ions in Table 5.1.1. First, each element that forms a cation is a metal, except for one (hydrogen), while each element that forms an anion is a nonmetal. This is actually one of the chemical properties of metals and nonmetals: metals tend to form cations, while nonmetals tend to form anions. Second, most atoms form ions of a single characteristic charge. When sodium atoms form ions, they always form a 1+ charge, never a 2+ or 3+ or even 1− charge. Thus, if you commit the information in Table 5.1.1 to memory, you will always know what charges most atoms form.

Table 5.1.1: Monatomic Ions of Various Charges

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

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

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

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

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

Example 5.1.1

Name each species.

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

Solution

a. This species has a 2− charge on it, so it is an anion. Anions are named using the stem of the element name with the suffix *-ide* added. This is the oxide anion.
b. Because this species has no charge, it is an atom in its elemental form. This is cobalt.
c. In this case, there is a 2+ charge on the atom, so it is a cation. We note from Table **5.1.1** that cobalt cations can have two possible charges, so the name of the ion must specify which charge the ion has. This is the cobalt(II) cation.

Exercise 5.1.1

Name each species.

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

Answers

a. the phosphide anion
b. the strontium cation

Ionic Formulas

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

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

the compound between Na^+ and Cl^-, we have the ionic formula NaCl (Figure **5.1.1**). The formula Na_2Cl_2 also has balanced charges, but the convention is to use the lowest ratio of ions, which would be one of each. (Remember from our conventions for writing formulas that we do not write a 1 subscript if there is only one atom of a particular element present.) For the ionic compound between magnesium cations (Mg^{2+}) and oxide anions (O^{2-}), again we need only one of each ion to balance the charges. By convention, the formula is MgO.



Figure **5.1.1**: The ionic compound **NaCl** is table salt and is very common. (Public Domain; Pexels.)

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

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

✔ Example 5.1.2

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

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

Solution

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

? Exercise 5.1.2

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

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

Answers

a. FeS
b. Fe_2S_3

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

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

Example 5.1.3

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. Co_2O_3

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride. It is *not* calcium(II) chloride, because calcium forms only one cation when it forms an ion, and it has a characteristic charge of 2+.
b. The name of this ionic compound is aluminum fluoride.
c. We know that cobalt can have more than one possible charge; we just need to determine what it is. Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−. This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. Therefore, the proper name for this ionic compound is cobalt(III) oxide.

Exercise 5.1.3

Name each ionic compound.

a. Sc_2O_3
b. AgCl

Answers

a. scandium oxide
b. silver chloride

How do you know whether a formula—and by extension, a name—is for a molecular compound or for an ionic compound? Molecular compounds form between nonmetals and nonmetals, while ionic compounds form between metals and nonmetals. The periodic table can be used to determine which elements are metals and nonmetals.

There also exists a group of ions that contain more than one atom. These are called **polyatomic ions**. Table 5.1.2 lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as ***oxyanions***. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge.

Table 5.1.2: Common Polyatomic Ions

Name	Formula and Charge		Name	Formula and Charge
ammonium	NH_4^+		hydroxide	OH^-
acetate	$C_2H_3O_2^-$, or CH_3COO^-		nitrate	NO_3^-
bicarbonate (hydrogen carbonate)	HCO_3^-		nitrite	NO_2^-
bisulfate (hydrogen sulfate)	HSO_4^-		peroxide	O_2^{2-}
carbonate	CO_3^{2-}		perchlorate	ClO_4^-
chlorate	ClO_3^-		phosphate	PO_4^{3-}
chromate	CrO_4^{2-}		sulfate	SO_4^{2-}
cyanide	CN^-		sulfite	SO_3^{2-}
dichromate	$Cr_2O_7^{2-}$		triiodide	I_3^-

The naming of ionic compounds that contain polyatomic ions follows the same rules as the naming for other ionic compounds: simply combine the name of the cation and the name of the anion. Do not use numerical prefixes in the name if there is more than one polyatomic ion; the only exception to this is if the name of the ion itself contains a numerical prefix, such as dichromate or triiodide.

Writing the formulas of ionic compounds has one important difference. If more than one polyatomic ion is needed to balance the overall charge in the formula, enclose the formula of the polyatomic ion in parentheses and write the proper numerical subscript to the right and *outside* of the parentheses. Thus, the formula between calcium ions, Ca^{2+}, and nitrate ions, NO_3^-, is properly written $Ca(NO_3)_2$, not $CaNO_{32}$ or CaN_2O_6. Use parentheses where required. The name of this ionic compound is simply calcium nitrate.

✔ Example 5.1.4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and S^{2-}
b. Al^{3+} and PO_4^{3-}
c. Fe^{2+} and PO_4^{3-}

Solution

a. Because the ammonium ion has a 1+ charge and the sulfide ion has a 2− charge, we need two ammonium ions to balance the charge on a single sulfide ion. Enclosing the formula for the ammonium ion in parentheses, we have $(NH_4)_2S$. The compound's name is ammonium sulfide.
b. Because the ions have the same magnitude of charge, we need only one of each to balance the charges. The formula is $AlPO_4$, and the name of the compound is aluminum phosphate.
c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, we need three iron(II) ions, and to get 6−, we need two phosphate ions. The proper formula is $Fe_3(PO_4)_2$, and the compound's name is iron(II) phosphate.

? Exercise 5.1.4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and PO_4^{3-}
b. Co^{3+} and NO_2^-

Answers

a. $(NH_4)_3PO_4$, ammonium phosphate

b. $Co(NO_2)_3$, cobalt(III) nitrite

Food and Drink Application: Sodium in Your Food

The element sodium, at least in its ionic form as Na^+, is a necessary nutrient for humans to live. In fact, the human body is approximately 0.15% sodium, with the average person having one-twentieth to one-tenth of a kilogram in their body at any given time, mostly in fluids outside cells and in other bodily fluids.

Sodium is also present in our diet. The common table salt we use on our foods is an ionic sodium compound. Many processed foods also contain significant amounts of sodium added to them as a variety of ionic compounds. Why are sodium compounds used so much? Usually sodium compounds are inexpensive, but, more importantly, most ionic sodium compounds dissolve easily. This allows processed food manufacturers to add sodium-containing substances to food mixtures and know that the compound will dissolve and distribute evenly throughout the food. Simple ionic compounds such as sodium nitrite ($NaNO_2$) are added to cured meats, such as bacon and deli-style meats, while a compound called sodium benzoate is added to many packaged foods as a preservative. Table **5.1.3** is a partial list of some sodium additives used in food. Some of them you may recognize after reading this chapter. Others you may not recognize, but they are all ionic sodium compounds with some negatively charged ion also present.

Table **5.1.3**: Some Sodium Compounds Added to Food

Sodium Compound	Use in Food
Sodium acetate	preservative, acidity regulator
Sodium adipate	food acid
Sodium alginate	thickener, vegetable gum, stabilizer, gelling agent, emulsifier
Sodium aluminum phosphate	acidity regulator, emulsifier
Sodium aluminosilicate	anti-caking agent
Sodium ascorbate	antioxidant
Sodium benzoate	preservative
Sodium bicarbonate	mineral salt
Sodium bisulfite	preservative, antioxidant
Sodium carbonate	mineral salt
Sodium carboxymethylcellulose	emulsifier
Sodium citrates	food acid
Sodium dehydroacetate	preservative
Sodium erythorbate	antioxidant
Sodium erythorbin	antioxidant
Sodium ethyl para-hydroxybenzoate	preservative
Sodium ferrocyanide	anti-caking agent
Sodium formate	preservative
Sodium fumarate	food acid
Sodium gluconate	stabilizer
Sodium hydrogen acetate	preservative, acidity regulator
Sodium hydroxide	mineral salt
Sodium lactate	food acid
Sodium malate	food acid
Sodium metabisulfite	preservative, antioxidant, bleaching agent
Sodium methyl para-hydroxybenzoate	preservative
Sodium nitrate	preservative, color fixative
Sodium nitrite	preservative, color fixative
Sodium orthophenyl phenol	preservative
Sodium propionate	preservative
Sodium propyl para-hydroxybenzoate	preservative
Sodium sorbate	preservative
Sodium stearoyl lactylate	emulsifier

Sodium Compound	Use in Food
Sodium succinates	acidity regulator, flavor enhancer
Sodium salts of fatty acids	emulsifier, stabilizer, anti-caking agent
Sodium sulfite	mineral salt, preservative, antioxidant
Sodium sulfite	preservative, antioxidant
Sodium tartrate	food acid
Sodium tetraborate	preservative

The use of so many sodium compounds in prepared and processed foods has alarmed some physicians and nutritionists. They argue that the average person consumes too much sodium from his or her diet. The average person needs only about 500 mg of sodium every day; most people consume more than this—up to 10 times as much. Some studies have implicated increased sodium intake with high blood pressure; newer studies suggest that the link is questionable. However, there has been a push to reduce the amount of sodium most people ingest every day: avoid processed and manufactured foods, read labels on packaged foods (which include an indication of the sodium content), avoid oversalting foods, and use other herbs and spices besides salt in cooking.



Figure **5.1.2**: Food labels include the amount of sodium per serving. This particular label shows that there are 75 mg of sodium in one serving of this particular food item.

Key Takeaways

- Ions form when atoms lose or gain electrons.
- Ionic compounds have positive ions and negative ions.
- Ionic formulas balance the total positive and negative charges.
- Ionic compounds have a simple system of naming.
- Groups of atoms can have an overall charge and make ionic compounds.

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5.2: Chemical Bond



Figure 5.2.1 (Credit: Flickr: Amelia Wells; Source: https://www.flickr.com/photos/speculummundi/4896031682/(opens in new window); License: CC by 2.0(opens in new window))

Have you ever made cupcakes from scratch?

You mix together flour, sugar, eggs, and other ingredients to make the batter, put the batter into cupcake papers, and then put them into the oven to bake. The cupcakes that come out of the oven after baking are different from any of the individual ingredients that went into the batter. Like the ingredients that join together to make cupcakes, atoms of different elements can join together to form entirely different substances called compounds. In cupcakes, the eggs and other wet ingredients cause the dry ingredients to stick together. What causes elements to stick together in compounds? The answer is chemical bonds.

What Is a Chemical Bond?

A chemical bond is a force of attraction between atoms or ions. Bonds form when atoms share or transfer valence electrons. Valence electrons are the electrons in the outer energy level of an atom that may be involved in chemical interactions. Valence electrons are the basis of all chemical bonds.

Q: Why do you think that chemical bonds form?

A: Chemical bonds form because they give atoms a more stable arrangement of electrons.

Why Bonds Form

To understand why chemical bonds form, consider the common compound(opens in new window) known as water, or H_2O. It consists of two hydrogen (H) atoms and one oxygen (O) atom. As you can see in the on the left side of the figure below, each hydrogen atom has just one electron, which is also its sole valence electron. The oxygen atom has six valence electrons. These are the electrons in the outer energy level of the oxygen atom.

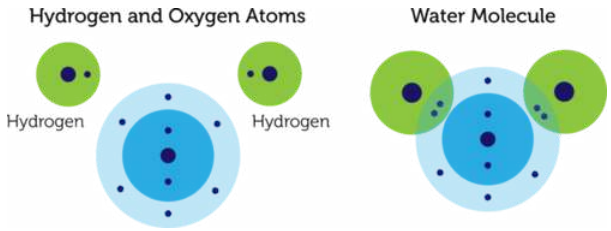


Figure 5.2.2: Copy and Paste Caption here. (Credit: Christopher AuYeung; Source: CK-12 Foundation; License: CC by-NC 3.0(opens in new window))

In the water molecule on the right in the figure above, each hydrogen atom shares a pair of electrons with the oxygen atom. By sharing electrons, each atom has electrons available to fill its sole or outer energy level. The hydrogen atoms each have a pair of shared electrons, so their first and only energy level is full. The oxygen atom has a total of eight valence electrons, so its outer energy level is full. A full outer energy level is the most stable possible arrangement of electrons. It explains why elements form chemical bonds with each other.

Types of Chemical Bonds

Not all chemical bonds form in the same way as the bonds in water. There are actually three different types of chemical bonds, called covalent, ionic, and metallic bonds. Each type of bond is described below.



- A covalent bond is the force of attraction that holds together two nonmetal atoms that share a pair of electrons. One electron is provided by each atom, and the pair of electrons is attracted to the positive nuclei of both atoms. The water molecule represented in Figure **5.2.2** contains covalent bonds.
- An ionic bond is the force of attraction that holds together oppositely charged ions. Ionic bonds form crystals instead of molecules. Table salt contains ionic bonds.
- A metallic bond is the force of attraction between a positive metal ion and the valence electrons that surround it—both its own valence electrons and those of other ions of the same metal. The ions and electrons form a lattice-like structure. Only metals, such as the copper pictured in Figure **5.2.3**, form metallic bonds.



Figure **5.2.3**: Metallic bonds explain many of the properties of metals. This coil of wire is made of the metal copper. Like other metals, copper is shiny, can be formed into wires, and conducts electricity. (Credit: Flavio~ - "Industrial Photography: Copper Wires-003"; Source: https://www.flickr.com/photos/37873897@N06/6154423015/(opens in new window); License: CC by 2.0(opens in new window))

Summary

- A chemical bond is a force of attraction between atoms or ions. Bonds form when atoms share or transfer valence electrons.
- Atoms form chemical bonds to achieve a full outer energy level, which is the most stable arrangement of electrons.
- There are three different types of chemical bonds: covalent, ionic, and metallic bonds.

Review

1. What is a chemical bond?
2. Explain why hydrogen and oxygen atoms are more stable when they form bonds in a water molecule.
3. How do ionic bonds and covalent bonds differ?

Explore More

Watch this video about covalent bonds, and then answer the questions below.



1. Which types of elements can form covalent bonds?
2. How can you tell the number of covalent bonds an element can form?
3. Why does one atom of nitrogen form bonds with three atoms of hydrogen?

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5.3: Covalent Bond

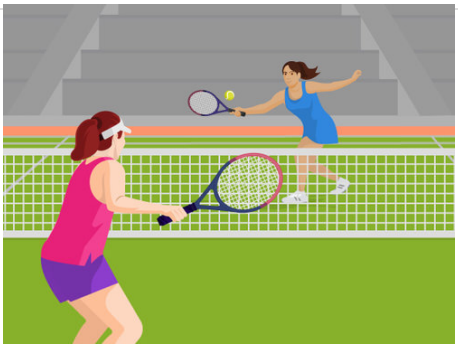


Figure 5.3.1 (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

In a tennis match, two players keep hitting the ball back and forth. The ball bounces from one player to the other, over and over again. The ball keeps the players moving together on the court. What if the two players represented the nuclei of two atoms and the ball represented valence electrons? What would the back and forth movement of the ball represent? The answer is a covalent bond.

Sharing Electrons

A covalent bond is the force of attraction that holds together two atoms that share a pair of valence electrons. The shared electrons are attracted to the nuclei of both atoms. This forms a molecule consisting of two or more atoms. Covalent bonds form only between atoms of nonmetals.

Covalent Compounds and Diatomic Elements

The two atoms that are held together by a covalent bond may be atoms of the same element or different elements. When atoms of different elements form covalent bonds, a new substance, called a covalent compound, results. Water is an example of a covalent compound. A water molecule is modeled in the figure below. A molecule is the smallest particle of a covalent compound that still has the properties of the compound.

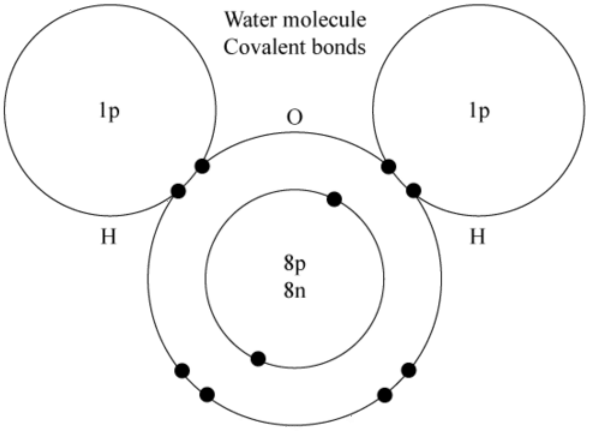


Figure 5.3.2 (Credit: Zachary Wilson; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Q: How many valence electrons does the oxygen atom (O) share with each hydrogen atom (H)? How many covalent bonds hold the water molecule together?

A: The oxygen atom shares one pair of valence electrons with each hydrogen atom. Each pair of shared electrons represents one covalent bond, so two covalent bonds hold the water molecule together.

The diagram in the figure below shows an example of covalent bonds between two atoms of the same element, in this case two atoms of oxygen. The diagram represents an oxygen molecule, so it's not a new compound. Oxygen normally occurs in diatomic ("two-atom") molecules. Several other elements also occur as diatomic molecules: hydrogen, nitrogen, and all but one of the halogens (fluorine, chlorine, bromine, and iodine).

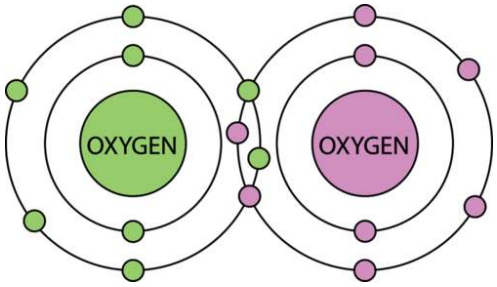


Figure **5.3.3** (Credit: Christopher AuYeung; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Q: How many electrons do these two oxygen atoms share? How many covalent bonds hold the oxygen molecule together?

A: The two oxygen atoms share two pairs of electrons, so two covalent bonds hold the oxygen molecule together.

Why Covalent Bonds Form

Covalent bonds form because they give atoms a more stable arrangement of electrons. Look at the oxygen atoms in the figure above. Alone, each oxygen atom has six valence electrons. By sharing two pairs of valence electrons, each oxygen atom has a total of eight valence electrons. This fills its outer energy level, giving it the most stable arrangement of electrons. The shared electrons are attracted to both oxygen nuclei, and this force of attraction holds the two atoms together in the oxygen molecule.

Summary

- A covalent bond is the force of attraction that holds together two atoms that share a pair of valence electrons. Covalent bonds form only between atoms of nonmetals.
- The two atoms that are held together in a covalent bond may be atoms of the same element or different elements. When atoms of different elements bond together, it forms a covalent compound.
- Covalent bonds form because the shared electrons fill each atom's outer energy level and this is the most stable arrangement of electrons.

Review

1. What is a covalent bond?
2. Nitrogen is a diatomic element with five valence electrons. Create a model of a molecule of nitrogen.
3. Which of the following represents a covalent compound?
    a. O_2
    b. CO_2
    c. Cl_2
    d. NaCl

Explore More

Watch the video about covalent bonding and then answer the questions below.



1. How can you tell the number covalent bonds the atoms of an element can form?
2. How many covalent bonds can nitrogen form? How many covalent bonds can chlorine form?
3. Why are covalent bonds stronger than ionic bonds?
4. Why can’t molecules of a covalent compound conduct electricity?

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5.4: Molecular Compounds



Figure **5.4.1** (Credit: Flickr: Timothy Vollmer; Source: https://www.flickr.com/photos/sixteenmilesofstring/2400018800/(opens in new window); License: CC by 2.0(opens in new window))

The burner on a gas stove burns with a pretty blue flame like the one pictured in the opening image. The fuel burned by most gas stoves is natural gas, which consists mainly of methane. Methane is a compound that contains only carbon and hydrogen. Like many other compounds that consist of just these two elements, methane is used for fuel because it burns very easily. Methane is an example of a covalent compound.

What Are Covalent Compounds?

Compounds that form from two or more nonmetallic elements, such as carbon and hydrogen, are called covalent compounds. In a covalent compound, atoms of the different elements are held together in molecules by covalent bonds. These are chemical bonds in which atoms share valence electrons. The force of attraction between the shared electrons and the positive nuclei of both atoms holds the atoms together in the molecule. A molecule is the smallest particle of a covalent compound that still has the properties of the compound.

The largest, most complex covalent molecules have thousands of atoms. Examples include proteins and carbohydrates, which are compounds in living things. The smallest, simplest covalent compounds have molecules with just two atoms. An example is hydrogen chloride (HCl). It consists of one hydrogen atom and one chlorine atom, as you can see in the figure below.

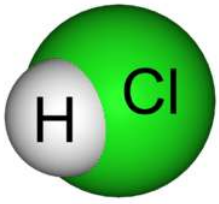


Figure **5.4.2** (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Hydrogen-chloride-3D-vdW-labelled.png(opens in new window); License: Public Domain)

Naming and Writing Formulas for Covalent Compounds

To name simple covalent compounds, follow these rules:

- Start with the name of the element closer to the left side of the periodic table.
- Follow this with the name of element closer to the right of the periodic table. Give this second name the suffix *–ide*.
- Use prefixes to represent the numbers of the different atoms in each molecule of the compound. The most commonly used prefixes are shown in the Table below.

Table **5.4.1**

Naming and Writing Formulas for Covalent Compounds

Number	Prefix
1	*mono-* (or none)
2	*di-*
3	*tri-*
4	*tetra-*
5	*penta-*
6	*hexa-*

Q: What is the name of the compound that contains three oxygen atoms and two nitrogen atoms?

A: The compound is named dinitrogen trioxide. Nitrogen is named first because it is farther to the left in the periodic table than oxygen. Oxygen is given the *-ide* suffix because it is the second element named in the compound. The prefix *di-* is added to nitrogen to show that there are two atoms of nitrogen in each molecule of the compound. The prefix *tri-* is added to oxygen to show that there are three atoms of oxygen in each molecule.

In the chemical formula for a covalent compound, the numbers of the different atoms in a molecule are represented by subscripts. For example, the formula for the compound named carbon dioxide is CO_2.

Q: What is the chemical formula for dinitrogen trioxide?

A: The chemical formula is N_2O_3.

Properties of Covalent Compounds

The covalent bonds of covalent compounds are responsible for many of the properties of the compounds. Because valence electrons are shared in covalent compounds, rather than transferred between atoms as they are in ionic compounds, covalent compounds have very different properties than ionic compounds.

- Many covalent compounds, especially those containing carbon and hydrogen, burn easily. In contrast, many ionic compounds do not burn.
- Many covalent compounds do not dissolve in water, whereas most ionic compounds dissolve well in water.
- Unlike ionic compounds, covalent compounds do not have freely moving electrons, so they cannot conduct electricity.
- The individual molecules of covalent compounds are more easily separated than the ions in a crystal, so most covalent compounds have relatively low boiling points. This explains why many of them are liquids or gases at room temperature. You can compare the boiling points of some covalent and ionic compounds in the Table below.

Table **5.4.2**

Properties of Covalent Compounds

Name of Compound(Chemical Formula)	Type of Compound	Boiling Point (°C)
Methane (CH4)	covalent	-164
Nitrogen oxide (NO)	covalent	-152
Sodium chloride (NaCl)	ionic	1413
Lithium fluoride (LiF)	ionic	1676

Q: The two covalent compounds in the table are gases at room temperature, which is 20°C. For a compound to be a liquid at room temperature, what does its boiling point have to be?

A: To be a liquid at room temperature, a covalent compound has to have a boiling point higher than 20°C. Water is an example of a covalent compound that is a liquid at room temperature. The boiling point of water is 100°C.

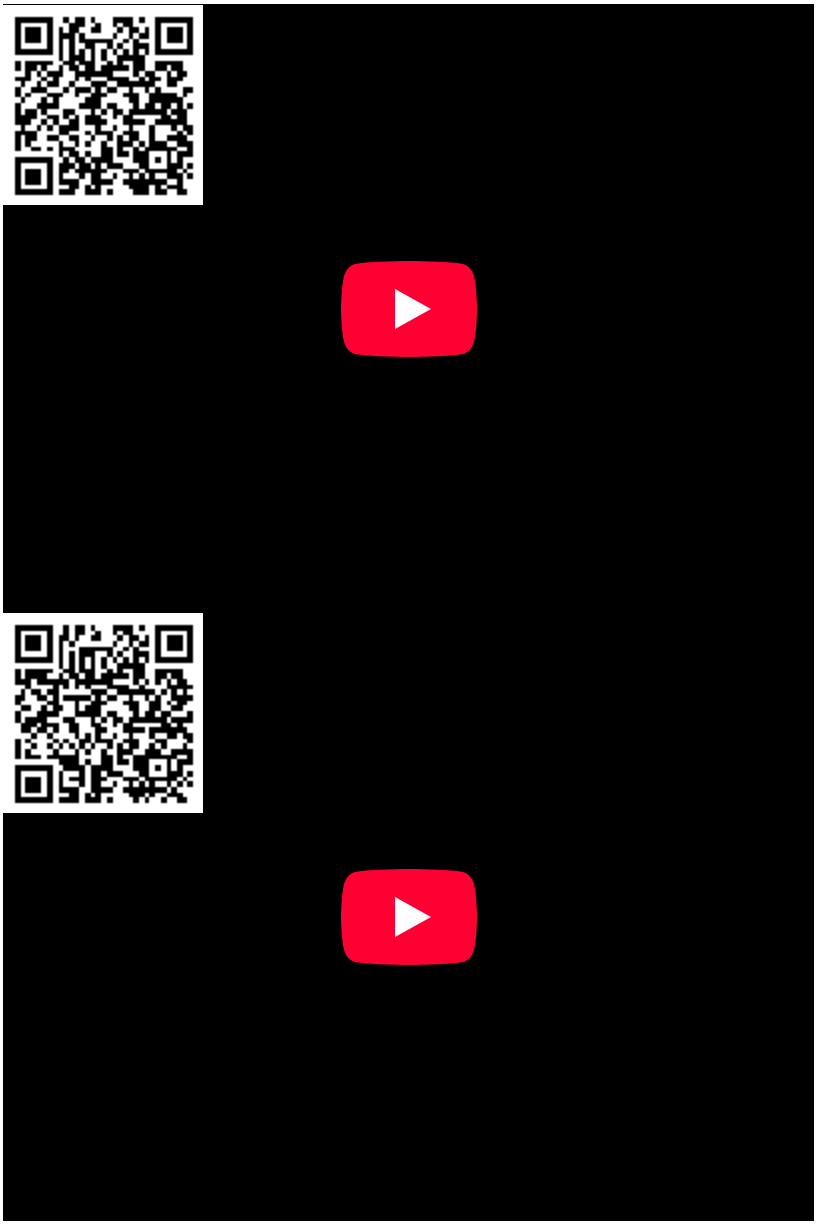
Summary

- Covalent compounds contain two or more nonmetallic elements held together by covalent bonds, in which atoms share pairs of valence electrons. A molecule is the smallest particle of a covalent compound that still has the properties of the compound.
- A few rules can be applied to name simple covalent compounds: name the left-most element in the periodic table first, add *-ide* to the second named element, and use prefixes for the numbers of atoms.
- Covalent bonds are responsible for many of the properties of covalent compounds. Covalent compounds have relatively low boiling points, cannot conduct electricity, and may not dissolve in water.

Review

1. What are covalent compounds? Give two examples.
2. What is the name of the covalent compound that consists of two atoms of silicon and six atoms of bromine? What is its chemical formula?
3. Compare and contrast the properties of ionic and covalent compounds.

Resources



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5.5: Energy and Covalent Bond Formation



Figure 5.5.1 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Why do $BeCl_2$ and LiCl bond differently?

We have learned that halide salts of elements in group 1 are typically ionic compounds. We would expect $LiCl$ to exist as Li^+ cations and Cl^- anions (and it does). However, if we move one column to the right, lithium's neighbor beryllium forms a different type of bond altogether. This bond consists of shared electrons between the Be and Cl atoms, not electrostatic attraction among ions.

Energy and Covalent Bond Formation

Molecular compounds are those that take the form of an individual molecule. Molecular compounds are generally comprised of two or more nonmetal atoms. Familiar examples include water (H_2O), carbon dioxide (CO_2), and ammonia (NH_3). Recall that the molecular formula shows the number of each atom that occurs in a molecule of that compound. One molecule of water contains two hydrogen atoms and one oxygen atom. Hydrogen (H_2) is an example of an element that exists naturally as a diatomic molecule. A **diatomic molecule** is a molecule containing two atoms.

Most atoms attain a lower potential energy when they are bonded to other atoms than when they are separated. Consider two isolated hydrogen atoms that are separated by a distance large enough to prevent any interaction between them. At this distance, the potential energy of the system is said to be equal to zero (see figure below).

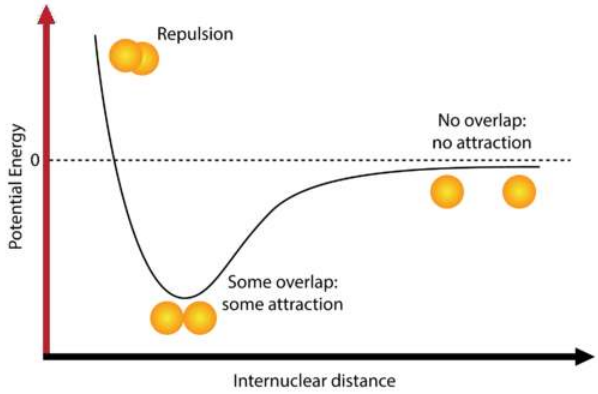


Figure 5.5.2: The graph shows how the potential energy of two hydrogen atoms changes as a function of their separation distance. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

As the atoms approach one another, their electron clouds gradually begin to overlap. Now there are several interactions which begin to occur. One is that the single electrons that each hydrogen atom possesses begin to repel each other. This repulsive force would tend to make the potential energy of the system increase. However, the electron of each atom begins to be attracted to the nucleus of the other atom. This attractive force tends to make the potential energy of the system decrease.

As the atoms first begin to interact, the attractive force is stronger than the repulsive force and so the potential energy of the system decreases, as seen in the diagram. Remember that the lower potential energy increases the stability of the system. As the two hydrogen atoms move closer and closer together, the potential energy is at its lowest possible point. If the hydrogen atoms move any closer together, a third interaction begins to dominate, and that is the repulsive force between the two positively-charged nuclei. This repulsive force is very strong, as can be seen by the sharp rise in energy at the far left of the diagram.

The point at which the potential energy reached its minimum represents the ideal distance between hydrogen atoms for a stable chemical bond to occur. This type of chemical bond is called a covalent bond. A **covalent bond** is a bond in which two atoms share one or more pairs of electrons. The single electrons from each of the two hydrogen atoms are shared when the atoms come together to form a hydrogen molecule (H_2).



Summary

- Covalent bonds are formed when atoms share electrons between them.

Review

1. What is a diatomic molecule?
2. What does lower potential energy do to a system?
3. What is the ideal distance for two atoms?

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5.6: Lewis Electron-Dot Structures

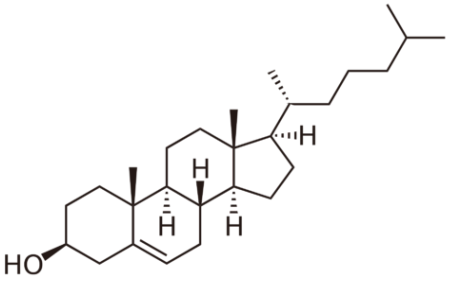


Figure
5.6.1
(Credit: User:BorisTM/Wikimedia Commons; Source:
http://commons.wikimedia.org/wiki/File:Cholesterol.svg(opens in new window)
; License: Public Domain).

What does cholesterol really look like?

We can write the structure of the cholesterol molecule a couple of different ways. The simplest approach is to simply write $C_{27}H_{46}O$. This "structure" is not very useful because it does not tell us how the carbons, hydrogens, and oxygen are connected to one another. The structure in the figure above is much more helpful—we see how the different atoms are connected together to form the molecule.

Lewis Electron-Dot Structures

In a previous chapter, you learned that the valence electrons of an atom can be shown in a simple way with an electron dot diagram. A hydrogen atom is shown as $H\cdot$ because of its one valence electron. The structures of molecules that are held together by covalent bonds can be diagrammed by **Lewis electron-dot structures**. The hydrogen molecule is shown in the figure below.

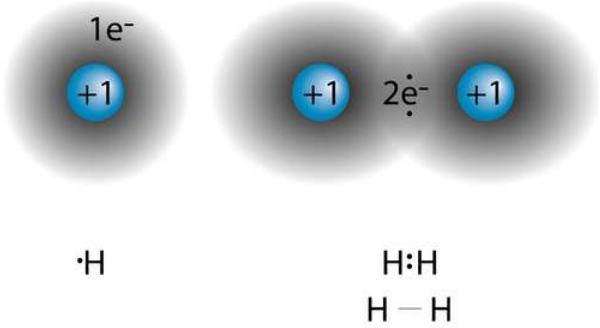


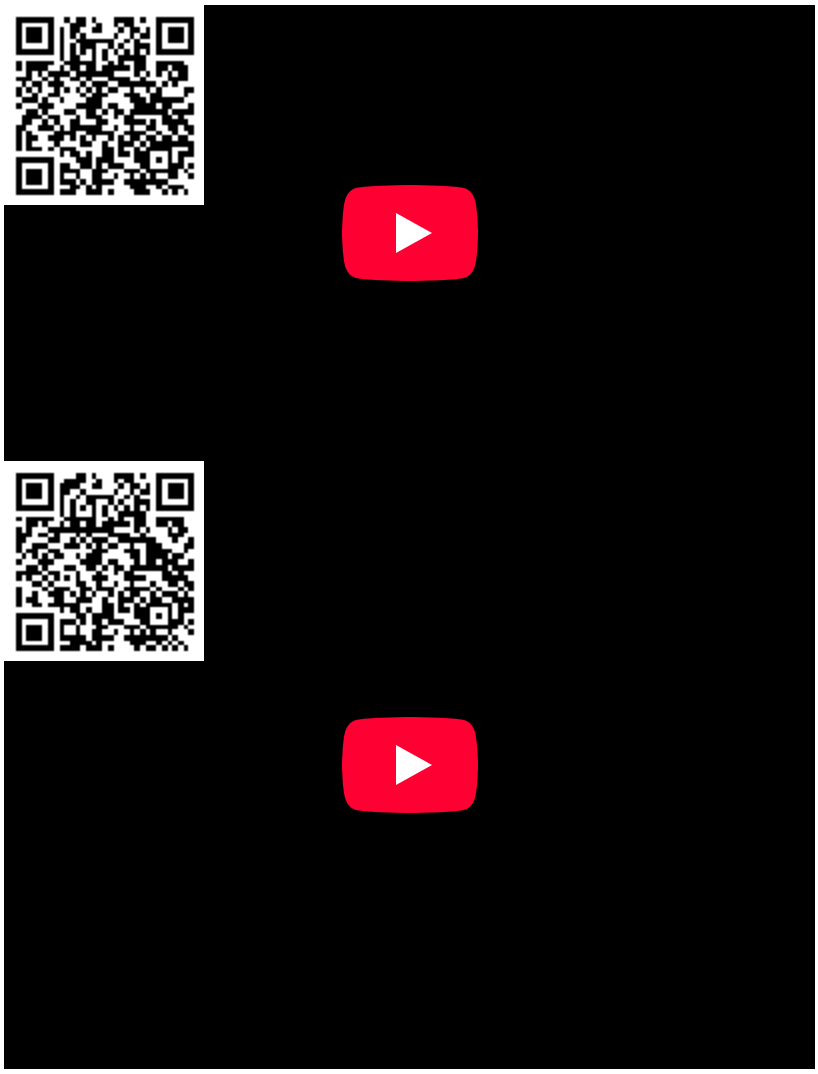
Figure **5.6.2**: On the left is a single hydrogen atom with one electron. On the right is an H_2 molecule showing the electron cloud overlap. (Credit: Jodi So; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The shared pair of electrons is shown as two dots in between the two H symbols ($H:H$). This is called a **single covalent bond**, when two atoms are joined by the sharing of one pair of electrons. The single covalent bond can also be shown by a dash in between the two symbols ($H—H$). A **structural formula** is a formula that shows the arrangement of atoms in a molecule and represents covalent bonds between atoms by dashes.

The Octet Rule and Covalent Bonds

When ions form, they conform to the **octet rule** by either losing or gaining electrons in order to achieve the electron configuration of the nearest noble gas. In a similar way, nonmetal atoms share electrons in the formation of a covalent bond in such a way that each of the atoms involved in the bond can attain a noble-gas electron configuration. The shared electrons are "counted" for each of the atoms involved in the sharing. For hydrogen (H_2), the shared pair of electrons means that each of the atoms is able to attain the

electron configuration of helium, the noble gas with two electrons. For atoms other than hydrogen, the sharing of electrons will usually provide each of the atoms with eight valence electrons.



Summary

- Lewis electron-dot structures show the bonding in covalent molecules.
- Covalent bonds between atoms can be indicated either with dots (:) or a dash (–).

Review

1. What is a single covalent bond?
2. How can covalently-bound atoms obey the octet rule?
3. Does the hydrogen molecule obey the octet rule?

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5.7: Single Covalent Bonds

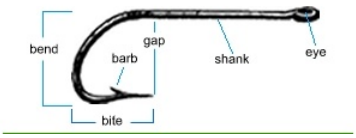


Figure 5.7.1 (Credit: Courtesy of the US Department of the Interior; Source: Commons Wikimedia, Fishhook(opens in new window) [commons.wikimedia.org]; License: Public Domain)

What holds molecules together?

In one form or another, the idea of atoms connecting to form larger substances has been with us for a long time. The Greek philosopher Democritus (460-370 BCE) believed that atoms had hooks that allowed them to connect with one another. Today, we believe that atoms are held together by bonds formed when two atoms share a set of electrons—a much more complicated picture than the simple hooks that Democritus believed in.

Single Covalent Bonds

A covalent bond forms when two orbitals with one electron each overlap one another. For the hydrogen molecule, this can be shown as:

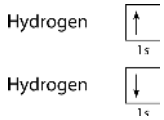


Figure 5.7.2 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Upon formation of the H_2 molecule, the shared electrons must have opposite spin, so they are shown with opposite spin in the atomic $1s$ orbital.

The halogens also form single covalent bonds in their diatomic molecules. An atom of any halogen, such as fluorine, has seven valence electrons. Its unpaired electron is located in the $2p$ orbital.

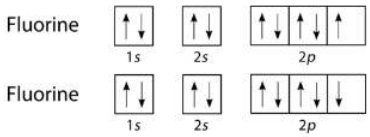


Figure 5.7.3 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The single electrons in the third $2p$ orbital combine to form the covalent bond:

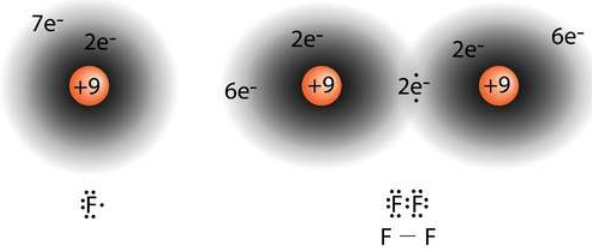


Figure 5.7.4: On the left is a fluorine atom with seven valence electrons. On the right is the F_2 molecule. (Credit: Jodi So; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The diatomic fluorine molecule (F_2) contains a single shared pair of electrons. Each F atom also has three pair of electrons that are not shared with the other atom. A **lone pair** is a pair of electrons in a Lewis electron-dot structure that is not shared between atoms. The oxygen atom in the water molecule shown below has two lone pair sets of electrons. Each F atom has three lone pairs. Combined with the two electrons in the covalent bond, each F atom follows the octet rule.



Example 5.7.1

Draw the Lewis electron dot structure for water.

Solution

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

Known

- Molecular formula of water $= \mathrm{H_2O}$
- 1 O atom $= 6$ valence electrons
- 2 H atoms $= 2 \times 1 = 2$ valence electrons
- Total number of valence electrons $= 8$

Use the periodic table to determine the number of valence electrons for each atom and the total number of valence electrons. Arrange the atoms and distribute the electrons so that each atom follows the octet rule. The oxygen atom will have 8 electrons, while the hydrogen atoms will each have 2.

Step 2: Solve.

Electron dot diagrams for each atom are:



Figure 5.7.5 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Each hydrogen atom with its single electron will form a covalent bond with the oxygen atom where it has a single electron. The resulting Lewis electron dot structure is:



Figure 5.7.6 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Step 3: Think about your result.

The oxygen atom follows the octet rule with two pairs of bonding electrons and two lone pairs. Each hydrogen atom follows the octet rule with one bonding pair of electrons.



Summary

- Covalent bonds form when electrons in two atoms form overlapping orbitals.
- Lone pair electrons in an atom are not shared with any other atom.

Review

1. How does a covalent bond form?
2. What relationship do the spins of shared electrons have with each other?
3. Do lone pair electrons form covalent bonds?

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5.8: Multiple Covalent Bonds

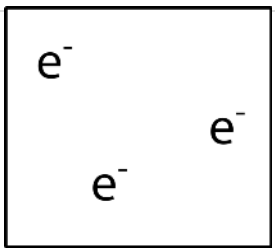


Figure 5.8.1 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

What do you do with your leftovers?

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

Multiple Covalent Bonds

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:

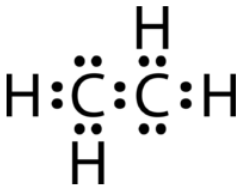


Figure 5.8.2: Incorrect dot structure of ethene. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

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 the carbon atoms share two pairs, instead of only one pair, of electrons.

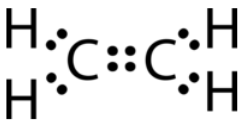


Figure 5.8.3: Correct dot structure for ethene. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

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.

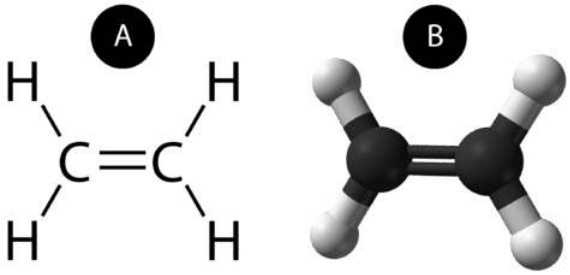


Figure 5.8.4: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: (A) http://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-dimensions-2D-Vector.svg(opens in new window); (B) http://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-3D-balls.png(opens in new window); License: Public Domain)

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.

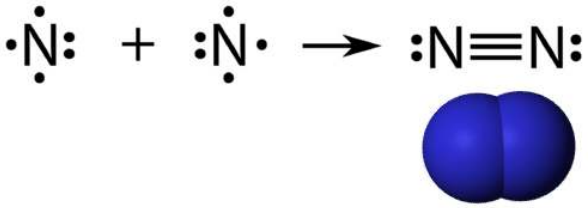


Figure 5.8.5: Triple bond in N_2. (Credit: CK-12 Foundation - Joy Sheng, using 3D molecular structure by Ben Mills (Wikimedia: Benjah-bmm27); Source: Molecular structure: http://commons.wikimedia.org/wiki/File:Nitrogen-3D-vdW.png(opens in new window); License: CC BY-NC-SA 3.0(opens in new window); Molecule Public Domain)

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.



Summary

- Lewis structures can be drawn for molecules that share multiple pairs of electrons.
- A double covalent bond is a covalent bond formed by atoms that share two pairs of electrons.
- A triple covalent bond is a covalent bond formed by atoms that share three pairs of electrons.

Review

1. Why is the first ethene Lewis structure incorrect?
2. What do the single electrons in nitrogen do to form a triple bond?
3. Draw the Lewis structure for ethyne C_2H_2.

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5.9: Bond Polarity



Figure 5.9.1 (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

What makes people share?

Have you ever spent time with someone you really didn't like? You had nothing in common with them and did not want to have anything to do with them. On the other hand, there are people that you enjoy being with. You have a lot in common and like to share with them. Atoms work the same way. If there are strong differences in their attraction of electrons, one atom gets the electrons and the other atom loses them. If they are similar, they share electrons to form a covalent bond.

Bond Polarity

Electronegativity is defined as the ability of an atom to attract electrons when the atoms are in a compound. Electronegativities of elements are shown in the periodic table below.

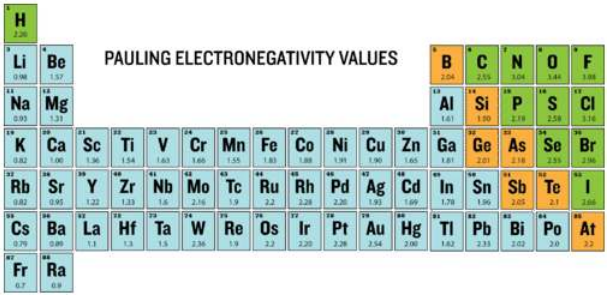


Figure 5.9.2: Electronegativities of elements. (Credit: Christopher Auyeung; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The degree to which a given bond is ionic or covalent is determined by calculating the difference in electronegativity between the two atoms involved in the bond.

As an example, consider the bond that occurs between an atom of potassium and an atom of fluorine. Using the table, the difference in electronegativity is equal to $4.0 - 0.8 = 3.2$. Since the difference in electronegativity is relatively large, the bond between the two atoms is ionic. Since the fluorine atom has a much larger attraction for electrons than the potassium atom does, the valence electron from the potassium atom is completely transferred to the fluorine atom. The diagram below shows how difference in electronegativity relates to the ionic or covalent character of a chemical bond.

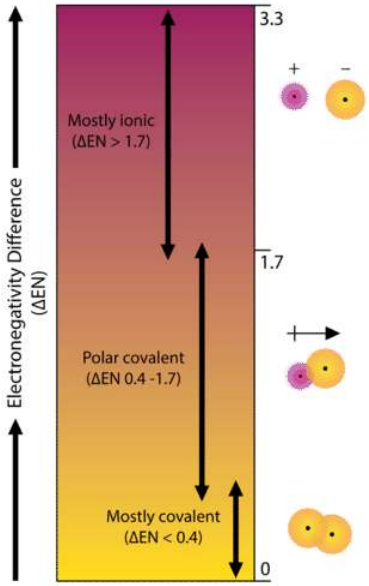


Figure **5.9.3**: Bond type is predicted on the difference in electronegativity of the two elements involved in the bond. (Credit: Zachary Wilson; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

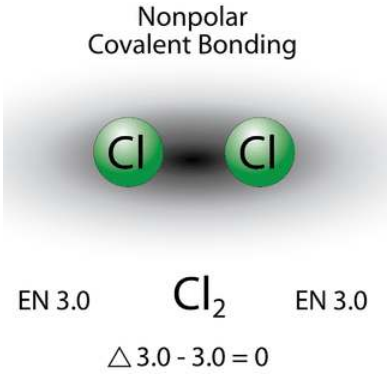


Figure **5.9.4**: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal. (Credit: Jodi So; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the $\mathbf{Cl_2}$ molecule is symmetrical. Note that molecules in which the electronegativity difference is very small (<0.4) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\mathbf{\Delta EN = 3.0 - 2.8 = 0.2}$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons, and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

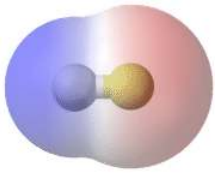


Figure 5.9.5: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: Commons Wikimedia, Hydrogen fluoride elpot transparent 3D balls (opens in new window) [commons.wikimedia.org]; License: Public Domain)

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

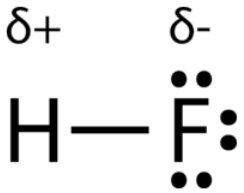


Figure 5.9.6: Use of δ to indicate partial charge. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

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

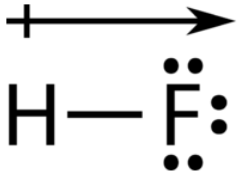


Figure 5.9.7: Use of crossed arrow to indicate polarity. (Credit: Joy Sheng
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Summary

- The electronegativity of an atom determines how strongly it attracts electrons to itself.
- The polarity of a bond is affected by the electronegativity values of the two atoms involved in that bond.

Review

1. If two atoms bonded together have an electronegativity difference of 1.9, what is the bond type?
2. What would be the bond type for BH_2?
3. Your friend tells you that the LiF bond is covalent. Are they correct? Why or why not.

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5.10: Polar Molecules

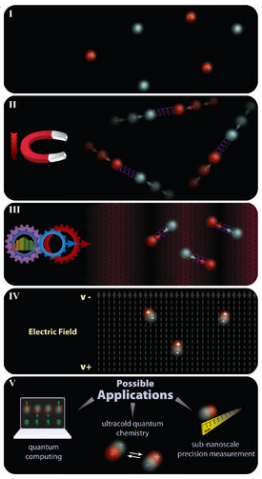


Figure 5.10.1 (Credit: Courtesy of G. Kuebler/JILA and the NIST; Source: Patapsco Image Gallery(opens in new window) [patapsco.nist.gov]; License: Public Domain)

How cold are ultracold polar molecules?

Ultracold polar molecules have been created by research scientists. These "molecules" consist of **Rb** and **K** atoms excited by lasers to form a type of **Rb–K** compound where the **Rb** has a positive charge and the **K** has a negative charge. The material is formed at temperatures extremely close to absolute zero. The researchers believe these techniques will help them make new reactions and new materials.

Polar Molecules

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 5.10.2: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule. (Credit: Christopher Auyeung; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Polar molecules orient themselves in the presence of an electric field with the positive ends of the molecule being attracted to the negative plate, while the negative ends of the molecules are attracted to the positive plate (see figure below).

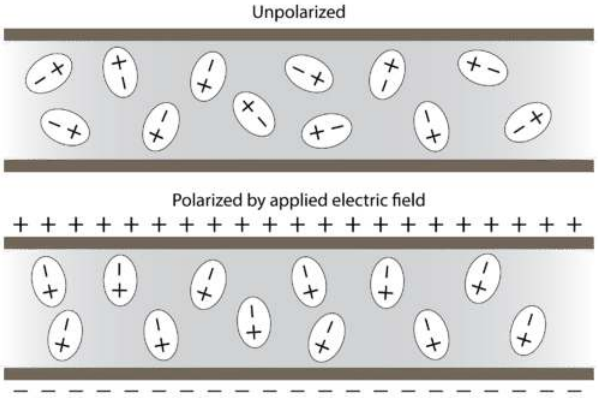


Figure 5.10.3: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves because of the attraction of opposite charges (bottom). (Credit: Zachary Wilson; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out, and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out, and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

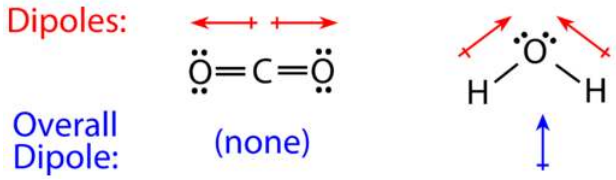


Figure 5.10.4: The molecular geometry of a molecule affects its polarity. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral H atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

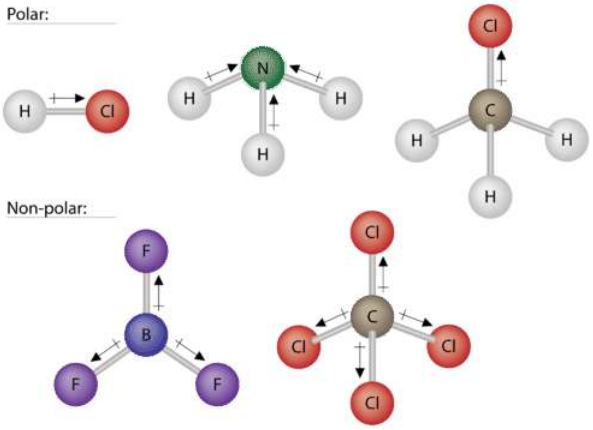


Figure 5.10.5: Some examples of polar and nonpolar molecules based on molecular geometry. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))



Summary

- Polar molecules result from differences in the electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

Review

1. Why is a polar molecule called a dipole?
2. The molecular geometry of NH_3 is trigonal pyramidal. What about the molecular geometry of NH_3 makes it a polar molecule?
3. What happens to polar molecules when an electric field is applied?

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5.11: VSEPR Theory

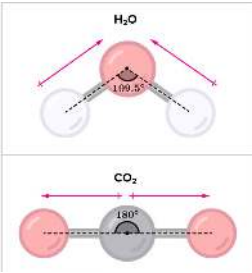


Figure **5.11.1**: Copy and Paste Caption here. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Why is the water molecule bent like that?

The characteristic bent shape of the water molecule shown above was a puzzling discovery for scientists at first. The shape allows the molecule to be polar, increasing its boiling point and making it possible for life on earth to exist as we know it. But what makes it bend? The structure is almost the same as carbon dioxide which is known to be a gas at room temperature, why not water too?

Putting atoms together to form compounds can be done on paper or in the lab. However, when the shape of the molecule made in the lab is different from the shape of the molecule drawn on paper, then we need to rethink our ideas and find better explanations.

VSEPR Theory

In 1956, British scientists R.J. Gillespie and R.S. Nyholm recognized that the current model for explaining bond angles did not work well. The theory at that time relied on hybrid orbitals to explain all aspects of bonding. The problem was that this theory gave an incorrect prediction of bond angles for many compounds. They developed a new approach based on earlier work by other scientists that incorporated a consideration of electron pairs in predicting three-dimensional structure.

The **valence shell** is the outermost electron-occupied shell of an atom. The valence shell holds the electrons that are involved in bonding and are the electrons shown in a Lewis structure. The acronym VSEPR stands for the **valence-shell electron pair repulsion** model. The model states that electron pairs will repel each other such that the shape of the molecule will adjust, so that the valence electron-pairs stay as far apart from one another as possible. Molecules can be systematically classified according to the number of bonding pairs of electrons; as well as the number of nonbonding, or lone pairs, around the central atom. For the purposes of the VSEPR model, a double or triple bond is no different in terms of repulsion than a single bond.



Summary

- VSEPR theory allows more accurate predictions of molecular shape.

Review

1. Who did the major work in developing the VSEPR theory?
2. Where are the electrons that are involved in bonding?
3. What is the basic idea behind the VSEPR theory?

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5.12: Molecular Shapes- No Lone Pairs on Central Atoms

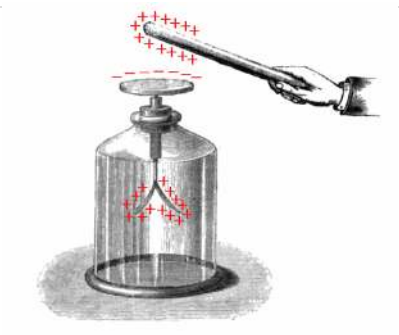


Figure 5.12.1 (Credit: Sylvanus P. Thompson; Source: http://commons.wikimedia.org/wiki/File:Electroscope_showing_induction.png(opens in new window); License: Public Domain)

How does an electroscope work?

An electroscope is a device used to study charge. When a positively charged object (the rod) nears the upper post, electrons flow to the top of the jar, leaving the two gold leaves positively charged. The leaves repel each other since both hold positive, like charges. The VSEPR theory says that electron pairs, also a set of like charges, will repel each other such that the shape of the molecule will adjust, so that the valence electron pairs stay as far apart from each other as possible.

Central Atom with No Lone Pairs

In order to easily understand the types of molecules possible, we will use a simple system to identify the parts of any molecule:

- A = **central atom** in a molecule
- B = atoms surrounding the central atom

Subscripts after the B will denote the number of B atoms that are bonded to the central A atom. For example, AB_4 is a molecule with a central atom surrounded by four covalently bonded atoms. Again, it does not matter if those bonds are single, double, or triple bonds.

AB_2: Beryllium Hydride (BeH_2)

Beryllium hydride consists of a central beryllium atom with two single bonds to hydrogen atoms. Recall that it violates the octet rule.

$$\mathbf{H{-}Be{-}H}$$

According to the requirement that electron pairs maximize their distance from one another, the two bonding pairs in the BeH_2 molecules will arrange themselves on directly opposite sides of the central **Be** atom. The resulting geometry is a linear molecule, shown in the figure below in a "ball and stick" model.



Figure 5.12.2: Beryllium hydride model. (Credit: Ben Mills (User:Benjah-bmm27/Wikimedia Commons); Source: http://commons.wikimedia.org/wiki/File:Beryllium-hydride-molecule-IR-3D-balls.png(opens in new window); License: Public Domain)

The bond angle from **H–Be–H** is **180°** because of its linear geometry.

Carbon dioxide is another example of a molecule which falls under the AB_2 category. Its Lewis structure consists of double bonds between the central carbon and the oxygen atoms (see figure below).

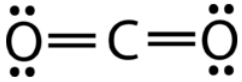


Figure 5.12.3: Carbon dioxide bonding. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The repulsion between the two groups of four electrons (two pairs) is no different than the repulsion of the two groups of two electrons (one pair) in the BeH_2 molecule. Carbon dioxide is also linear (see figure below).



Figure 5.12.4: Carbon dioxide. (Credit: User:Benji9072/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Carbon_dioxide_structure.png(opens in new window); License: Public Domain)

AB_3: Boron Trifluoride (BF_3)

Boron trifluoride consists of a central boron atom with three single bonds to fluorine atoms (see figure below). The boron atom also has an incomplete octet.

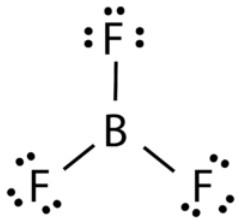


Figure 5.12.5: Boron trifluoride bonding. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The geometry of the BF_3 molecule is called trigonal planar (figure 5.12.3). The fluorine atoms are positioned at the vertices of an equilateral triangle. The F—B—F angle is 120° and all four atoms lie in the same plane.



Figure 5.12.6: Boron trifluoride model. (Credit: User:Benji9072/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Boron-trifluoride-3D-balls.png(opens in new window); License: Public Domain)

AB_4: Methane (CH_4)

Methane is an organic compound that is the primary component of natural gas. Its structure consists of a central carbon atom with four single bonds to hydrogen atoms (see figure below). In order to maximize their distance from one another, the four groups of bonding electrons do not lie in the same plane. Instead, each of the hydrogen atoms lie at the corners of a geometrical shape called a tetrahedron. The carbon atom is at the center of the tetrahedron. Each face of a tetrahedron is an equilateral triangle.

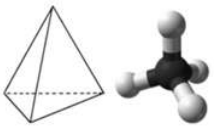


Figure 5.12.7: Tetrahedral structure of methane. (Credit: (Left) Pearson Scott Foresman; (Right) Ben Mills (Wikimedia: Benjah-bmm27); Source: (Left) http://commons.wikimedia.org/wiki/File:Tetrahedron_(PSF).png(opens in new window); (Right) http://commons.wikimedia.org/wiki/File:Methane-CRC-MW-3D-balls.png(opens in new window); License: Public Domain)

The molecular geometry of the methane molecule is tetrahedral (see figure 5.12.5). The H—C—H bond angles are 109.5°, which is larger than the 90° that they would be if the molecule was planar. When drawing a structural formula for a molecule such as methane, it is advantageous to be able to indicate the three-dimensional character of its shape. The structural formula below is called a perspective drawing. The dotted line bond is to be visualized as receding into the page, while the solid triangle bond is to be visualized as coming out of the page.

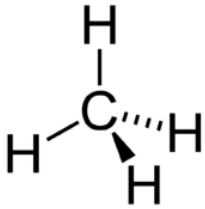


Figure 5.12.8: Methane perspective model. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Summary

- Electron pairs repel each other and influence bond angles and molecular shape.

Review

1. What are the bond angles in carbon dioxide?
2. What molecule has bond angles of 109.5°?
3. What is the geometry of the BF_3 molecule?

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5.13: Molecular Shapes - Lone Pair(s) on Central Atom



Figure 5.13.1 (Credit: Image copyright Jandrie Lombard, 2014; Source: http://www.shutterstock.com(opens in new window); License: Used under license from Shutterstock.com)

How can all these clothes fit into such a small space?

When we travel, we often take a lot more stuff than we need. Trying to fit it all into a suitcase can be a real challenge. We may have to repack or just squeeze it all in. Atoms often have to rearrange where the electrons are in order to create a more stable structure.

Central Atom with One or More Lone Pairs

The molecular geometries of molecules change when the central atom has one or more lone pairs of electrons. The total number of electron pairs, both bonding pairs and lone pairs, leads to what is called the **electron domain geometry**. When one or more of the bonding pairs of electrons is replaced with a lone pair, the molecular geometry (actual shape) of the molecule is altered. In keeping with the A and B symbols established in the previous section, we will use E to represent a lone pair on the central atom (A). A subscript will be used when there is more than one lone pair. Lone pairs on the surrounding atoms (B) do not affect the geometry.

AB_3E: Ammonia, NH_3

The ammonia molecule contains three single bonds and one lone pair on the central nitrogen atom (see figure below).

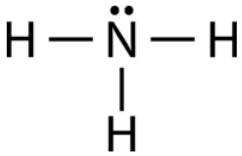


Figure 5.13.2: Lone pair electrons in ammonia. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The domain geometry for a molecule with four electron pairs is tetrahedral, as was seen with CH_4. In the ammonia molecule, one of the electron pairs is a lone pair rather than a bonding pair. The molecular geometry of NH_3 is called trigonal pyramidal (see figure below).

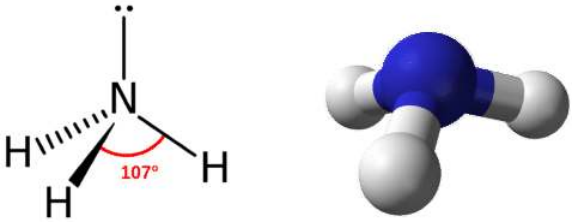


Figure 5.13.3: Ammonia molecule. (Credit: (Left) User: Booyabazooka/ Wikimedia Commons; (Right) Ben Mills (Wikimedia: Benjah-bmm27); Source: (Left) http://commons.wikimedia.org/wiki/File:Ammonia_lone_electron_pair.svg(opens in new window); (Right) http://commons.wikimedia.org/wiki/File:Ammonia-3D-balls-A.png(opens in new window); License: Public Domain)

Recall that the bond angle in the tetrahedral CH_4 molecule is $109.5°$. Again, the replacement of one of the bonded electron pairs with a lone pair compresses the angle slightly. The $H–N–H$ angle is approximately $107°$.

AB_2E_2: Water, H_2O

A water molecule consists of two bonding pairs and two lone pairs (see figure below).



Figure 5.13.4: Lone pair electrons on water. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

As for methane and ammonia, the domain geometry for a molecule with four electron pairs is tetrahedral. In the water molecule, two of the electron pairs are lone pairs rather than bonding pairs. The molecular geometry of the water molecule is bent. The H—O—H bond angle is 104.5°, which is smaller than the bond angle in NH_3 (see figure below).

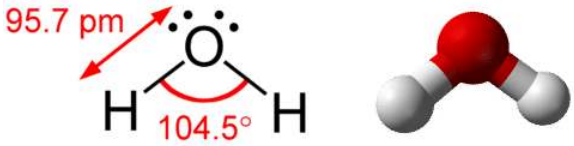


Figure 5.13.5: Water molecule. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: (Left) http://commons.wikimedia.org/wiki/File:Water-dimensions-from-Greenwood%2526Earnshaw-2D.png(opens in new window); (Right) http://commons.wikimedia.org/wiki/File:Water-3D-balls-A.png(opens in new window); http://commons.wikimedia.org/wiki/File:Zeepzieden.jpg(opens in new window); License: Public Domain)

AB_4E: Sulfur Tetrafluoride, SF_4

The Lewis structure for SF_4 contains four single bonds and a lone pair on the sulfur atom (see figure below).

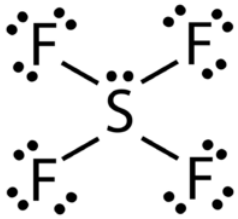


Figure 5.13.6: Lone pair electrons in SF_4. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The sulfur atom has five electron groups around it, which corresponds to the trigonal bipyramidal domain geometry, as in PCl_5 (see figure below). Recall that the trigonal bipyramidal geometry has three equatorial atoms and two axial atoms attached to the central atom. Because of the greater repulsion of a lone pair, it is one of the equatorial atoms that are replaced by a lone pair. The geometry of the molecule is called a distorted tetrahedron, or seesaw.



Figure 5.13.7: Ball and stick model for SF_4. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Sulfur-tetrafluoride-3D-balls.png(opens in new window); License: Public Domain)

Table 5.13.1: Geometries in Which the Central Atom Has One or More Lone Pairs

Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Electron Domain Geometry	Molecular Geometry	Examples
3	2	1	Trigonal Planar	Bent	O_3
4	3	1	Tetrahedral	Trigonal Pyramidal	NH_3
4	2	2	Tetrahedral	Bent	H_2O
5	4	1	Trigonal Bipyramidal	Distorted Tetrahedron (Seesaw)	SF_4
5	3	2	Trigonal Bipyramidal	T-shaped	ClF_3
5	2	3	Trigonal Bipyramidal	Linear	I_3^-
6	5	1	Octahedral	Square Pyramidal	BrF_5
6	4	2	Octahedral	Square Planar	XeF_4





Summary

- The presence of lone pair electrons influences the three-dimensional shape of the molecule.

Review

1. Why does water have a bent geometry?
2. Why is ammonia not a planar molecule?
3. How would we write the configuration for xenon tetrafluoride using the ABE system?

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5.14: Physical Properties and Intermolecular Forces



Figure 5.14.1 (Credit: Moskey71; Source: https://commons.wikimedia.org/wiki/File:HopeDiamond.JPG(opens in new window); License: Public Domain)

Can you guess how much this is worth?

Carbon is an interesting and versatile element. There are over twenty million known compounds containing carbon, encompassed in the growing field of organic chemistry. The element itself can exist in two major forms. Diamond is a form of carbon that is extremely hard and is one of the few materials that can scratch glass. The other form of carbon is graphite, a very soft material that we find in "lead" pencils. The two forms differ mainly in how the carbon atoms are connected to one another. The differences in the arrangement of atoms affect the properties of the material.

Physical Properties and Intermolecular Forces

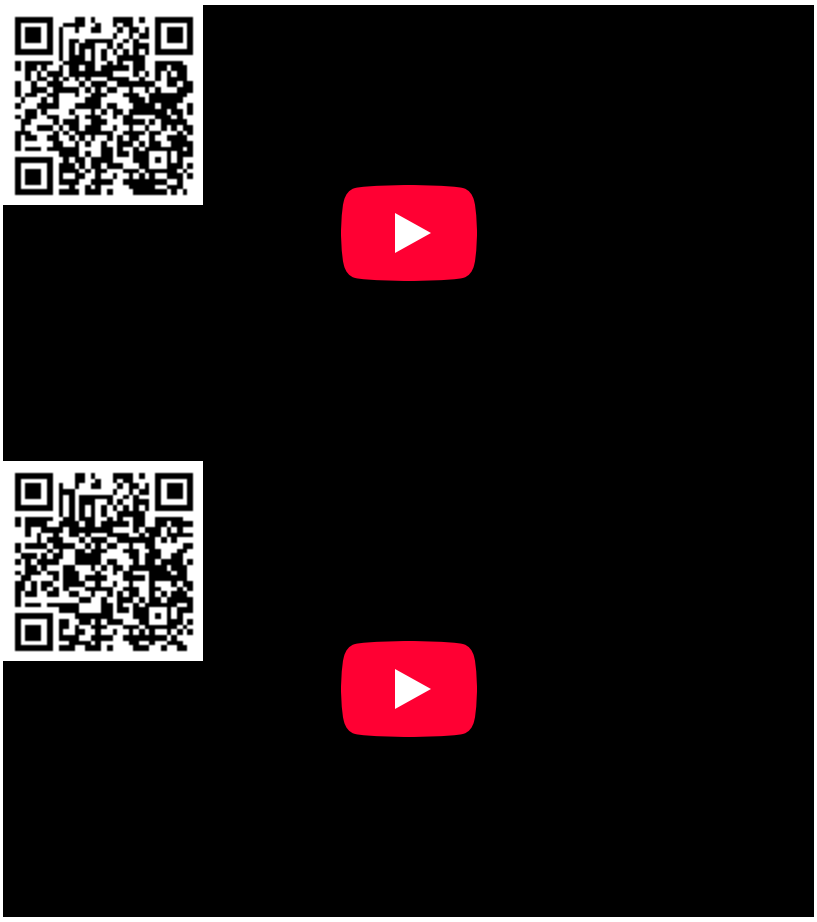
The physical state and properties of a particular compound depend in large part on the type of chemical bonding it displays. **Molecular compounds**, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions. The melting and boiling points of molecular compounds are generally quite low compared to those of **ionic compounds**. This is because the energy required to disrupt the **intermolecular forces** between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity in the solid state because of their rigid structure, but conduct well when either molten or dissolved into a solution. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The table below summarizes some of the differences between ionic and molecular compounds.

Table 5.14.1: Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	metal and nonmetal	nonmetals only
Bonding	ionic – transfer of electron(s) between atoms	covalent – sharing of pair(s) of electrons between atoms
Representative unit	formula unit	molecule
Physical state at room temp.	solid	gas, liquid, or solid
Water solubility	usually high	variable
Melting and boiling temps	generally high	generally low
Electrical conductivity	good when molten or in solution	poor

One type of molecular compound behaves quite differently than that described so far. A covalent network solid is a compound in which all of the atoms are connected to one another by covalent bonds. Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming

the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above 3500°C.



Summary

- The physical properties of a material are affected by the intermolecular forces holding the molecules together.

Review

1. Are melting points of molecular compounds generally higher or lower than those of ionic compounds?
2. Do ionic compounds conduct electricity in the solid state?
3. What types of substances are generally water-soluble?

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CHAPTER OVERVIEW

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6.1: Avogadro's Number



Figure 6.1.1 (Credit: User:OSX/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:1983-1988_Toyota_Hilux_4-door_utility_01.jpg(opens in new window); License: Public Domain)

Is there an easier way to load this truck?

When the weather is nice, many people begin to work on their yards and homes. For many projects, sand is needed as a foundation for a walk or to add to other materials. You could order up twenty million grains of sand and have people really stare at you. You could order by the pound, but that takes a lot of time weighing out. The best bet is to order by the yard, meaning a cubic yard. The loader can easily scoop up what you need and put it directly in your truck.

Avogadro's Number

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

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



Figure 6.1.2: Italian scientist Amadeo Avogadro, whose work led to the concept of the mole as a counting unit in chemistry. (Credit: C. Sentier; Source: http://commons.wikimedia.org/wiki/File:Amedeo_Avogadro2.jpg(opens in new window); License: Public Domain)

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



Figure **6.1.3**: The animal mole is very different than the counting unit of the mole. Chemists nonetheless have adopted the mole as their unofficial mascot. National Mole Day is a celebration of chemistry that occurs on October 23rd (10/23) of each year. (Credit: Left: Michael David Hill, 2005 (Mikiwikipikidikipedia); Right: chrisbb@prodigy.net;(left) Michael David Hill, 2005 (Mikiwikipikidikipedia); (right) chrisbb@prodigy.net; Source: Left: http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg(opens in new window); Right: http://www.flickr.com/photos/chrisbrenschmidt/436990097/(opens in new window); (left) http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg(opens in new window); (right) http://www.flickr.com/photos/chrisbrenschmidt/436990097/(opens in new window); License: (left) CC-BY 2.5; (right) CC-BY 2.0)



Summary

- A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.

Review

1. What is the SI unit for amount of a substance?
2. What is the representative particle for an element?
3. The formula unit is the representative particle for what?

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6.2: Conversions Between Moles and Atoms



Figure **6.2.1** (Credit: Courtesy of Diane A. Reid/National Cancer Institute; Source: http://commons.wikimedia.org/wiki/File:Man_responds_to_telephone_call.jpg(opens in new window); License: Public Domain)

Big numbers or little numbers?

Do you hate to type subscripts and superscripts? Even with a good word-processing program, having to click on an icon to get a superscript and then remembering to click off after you type the number can be a real hassle. If we did not know about moles and just knew about numbers of atoms or molecules (those big numbers that require lots of superscripts), life would be much more complicated and we would make many more typing errors.

Conversions Between Moles and Atoms

Conversions Between Moles and Number of Particles

Using our unit conversion techniques, we can use the mole label to convert back and forth between the number of particles and moles.

Example 6.2.1: Converting Number of Particles to Moles

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

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

Known

- number of C atoms $= 4.72 \times 10^{24}$
- 1 mole $= 6.02 \times 10^{23}$ atoms

Unknown

- 4.72 x 10^{24} = ? mol C

One conversion factor will allow us to convert from the number of C atoms to moles of C atoms.

Step 2: Calculate.

$$4.72 \times 10^{24}\ \text{atoms C} \times \frac{1\ \text{mol C}}{6.02 \times 10^{23}\ \text{atoms C}} = 7.84\ \text{mol C}$$

Step 3: 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.

Suppose that you want to know how many hydrogen atoms are in a mole of water molecules. First, you need to know the chemical formula for water, which is H_2O. There are two atoms of hydrogen in each molecule of water. How many atoms of hydrogen are in two water molecules? There are $2 \times 2 = 4$ hydrogen atoms. How about in a dozen? In that case, a dozen is 12; so $12 \times 2 = 24$

hydrogen atoms in a dozen water molecules. To get the answers (4 and 24), you multiply the given number of molecules by two atoms of hydrogen per molecule. So, to find the number of hydrogen atoms in a mole of water molecules, the problem can be solved using conversion factors:

$$1\ \text{mol}\ H_2O \times \frac{6.02 \times 10^{23}\ \text{molecules}\ H_2O}{1\ \text{mol}\ H_2O} \times \frac{2\ \text{atoms H}}{1\ \text{molecule}\ H_2O} = 1.20 \times 10^{24}\ \text{atoms H}$$

The first conversion factor converts from moles of particles to the number of particles. The second conversion factor reflects the number of atoms contained within each molecule.



Figure **6.2.2**: Two water molecules contain 4 hydrogen atoms and 2 oxygen atoms. A mole of water molecules contains 2 moles of hydrogen atoms and 1 mole of oxygen atoms. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Water-3D-balls-A.png(opens in new window); License: Public Domain)

Example 6.2.2: Atoms, Molecules, and Moles

Sulfuric acid has the chemical formula H_2SO_4. A certain quantity of sulfuric acid contains 4.89×10^{25} atoms of oxygen. How many moles of sulfuric acid is the sample?

Solution:

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

Known

- $4.89 \times 10^{25} = O$ atoms
- 1 mole $= 6.02 \times 10^{23}$ molecules H_2SO_4

Unknown

- mol of H_2SO_4 molecules

Two conversion factors will be used. First, convert atoms of oxygen to molecules of sulfuric acid. Then, convert molecules of sulfuric acid to moles of sulfuric acid.

Step 2: Calculate.

$$4.89 \times 10^{25}\ \text{atoms O} \times \frac{1\ \text{molecule}\ H_2SO_4}{4\ \text{atoms O}} \times \frac{1\ \text{mol}\ H_2SO_4}{6.02 \times 10^{23}\ \text{molecules}\ H_2SO_4} = 20.3\ \text{mol}\ H_2SO_4$$

Step 3: Think about your result.

The original number of oxygen atoms was about 80 times larger than Avogadro's number. Since each sulfuric acid molecule contains 4 oxygen atoms, there are about 20 moles of sulfuric acid molecules.



Summary

- Methods are described for conversions between moles, atoms, and molecules.

Review

1. What conversion factor would we need to convert moles of helium to atoms of helium?
2. I want to convert atoms to moles. My friend tells me to multiply the number of atoms by 6.02×10^{23} atoms/mole. Is my friend correct?
3. Why do you need to know the formula for a molecule in order to calculate the number of moles of one of the atoms?
4. How many atoms of fluorine are in 5.6×10^{22} molecules of MgF_2?

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6.3: Chemical Formulas as Conversion Factors

Learning Objectives

- Use chemical formulas as conversion factors.

Figure **6.3.1** 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.

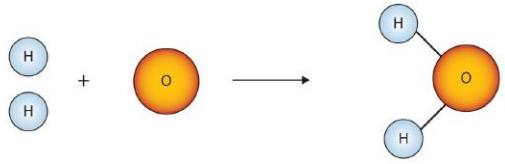


Figure **6.3.1** Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

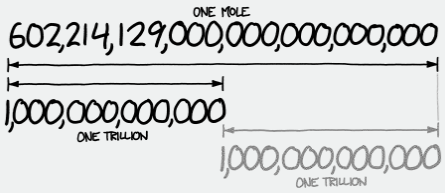
Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of water (H_2O) we can construct the relationships given in (Table **6.3.1**).

Table **6.3.1**: 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 **6.3.2**: 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 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 **6.3.2** as conversion factors.

Example 6.3.1: 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. $2.5\ \cancel{\text{mol }C_2H_6O\text{ molecules}} \times \frac{2\text{ mol C atoms}}{1\ \cancel{\text{mol }C_2H_6O\text{ molecules}}} = 5.0\text{ mol C atoms}$
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 6.3.1

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

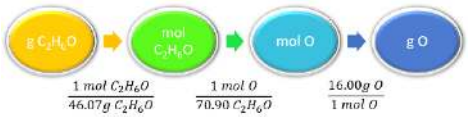
The fact that 1 mol equals 6.022×10^{23} items can also be used as a conversion factor.

Example 6.3.2: 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.	$75.0\ \cancel{g\ C_2H_6O} \times \frac{1\ \cancel{mol\ C_2H_6O}}{46.07\ \cancel{g\ C_2H_6O}} \times \frac{1\ \cancel{mol\ O}}{1\ \cancel{mol\ C_2H_6O}} \times \frac{16.00\ g\ O}{1\ \cancel{mol\ O}} = 26.0\ g$
Think about your result.	

Exercise 6.3.2

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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6.4: Molar Mass



Figure 6.4.1 (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Potassium-dichromate-sample.jpg(opens in new window); License: Public Domain)

When creating a solution, how do I know how much of each substance to put in?

I want to make a solution that contains 1.8 moles of potassium dichromate. You do not have a balance calibrated in moles, but you do have one calibrated in grams. If you know the relationship between moles and the number of grams in a mole, you can use your balance to measure out the needed amount of material.

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 lithium is $6.94\ \text{g}$, the molar mass of zinc is $65.38\ \text{g}$, and the molar mass of gold is $196.97\ \text{g}$. Each of these quantities contains 6.02×10^{23} atoms of that particular element. The units for molar mass are grams per mole, or g/mol.

Molar Masses of Compounds

The molecular formula of the compound carbon dioxide is CO_2. One molecule of carbon dioxide consists of 1 atom of carbon and 2 atoms of oxygen. We can calculate the mass of one molecule of carbon dioxide by adding together the masses of 1 atom of carbon and 2 atoms of oxygen:

$$12.01\ \text{amu} + 2\,(16.00\ \text{amu}) = 44.01\ \text{amu}$$

The **molecular mass** of a compound is the mass of one molecule of that compound. The molecular mass of carbon dioxide is $44.01\ \text{amu}$.

The molar mass of any compound is the mass in grams of one mole of that compound. One mole of carbon dioxide molecules has a mass of $44.01\ \text{g}$, while one mole of sodium sulfide formula units has a mass of $78.04\ \text{g}$. The molar masses are $44.01\ \text{g/mol}$ and $78.04\ \text{g/mol}$ respectively. In both cases, that is the mass of 6.02×10^{23} representative particles. The representative particle of CO_2 is the molecule, while for Na_2S it is the formula unit.

Example 6.4.1: Molar Mass of a Compound

Calcium nitrate, $Ca(NO_3)_2$, is used as a component in fertilizer. Determine the molar mass of calcium nitrate.

Solution

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

Known

- Formula $= Ca(NO_3)_2$
- Molar mass $Ca = 40.08\ \text{g/mol}$
- Molar mass $N = 14.01\ \text{g/mol}$
- Molar mass $O = 16.00\ \text{g/mol}$

Unknown

- molar mass $Ca(NO_3)_2$

First we need to analyze the formula. Since the **Ca** lacks a subscript, there is one **Ca** atom per formula unit. The 2 outside the parentheses means that there are two nitrate ions per formula unit and each nitrate ion consists of one nitrogen atom and three oxygen atoms per formula unit. Thus, **1 mol** of calcium nitrate contains **1 mol** of **Ca** atoms, **2 mol** of **N** atoms, and **6 mol** of **O** atoms.

Step 2: Calculate

Use the molar masses of each atom together with the number of atoms in the formula and add together.

$$1\ \text{mol Ca} \times \frac{40.08\ \text{g Ca}}{1\ \text{mol Ca}} = 40.08\ \text{g Ca}$$

$$2\ \text{mol N} \times \frac{14.01\ \text{g N}}{1\ \text{mol N}} = 28.02\ \text{g N}$$

$$6\ \text{mol O} \times \frac{16.00\ \text{g O}}{1\ \text{mol O}} = 96.00\ \text{g O}$$

Molar mass of $\text{Ca(NO}_3)_2 = 40.08\ \text{g} + 28.02\ \text{g} + 96.00\ \text{g} = 164.10\ \text{g/mol}$



Summary

- Calculations are described for the determination of molar mass of an atom or a compound.

Review

1. What is the molar mass of Pb?
2. Where do you find the molar mass of an element?
3. How many moles of Cl are in one mole of the $CaCl_2$?
4. How many moles of H are in one mole of the compound $(NH_4)_3PO_4$?
5. Calculate the molar mass of $CaCl_2$.

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6.5: Conversions Between Moles and Mass



Figure 6.5.1 (Credit: User:Estormiz/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Fermion_Plant_Oulu_2007_01_20.JPG(opens in new window); License: Public Domain)

How can we get more product?

Chemical manufacturing plants are always seeking to improve their processes. One way that improvement comes about is through measuring the amount of material produced in a reaction. By knowing how much is made, the scientists and engineers can try different ways of getting more product at less cost.

Conversions Between Moles and Mass

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment, you need 3.00 moles of calcium chloride ($\mathrm{CaCl_2}$). Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. The molar mass of $\mathrm{CaCl_2}$ is $110.98\ \mathrm{g/mol}$. The conversion factor that can be used is then based on the equality that $1\ \mathrm{mol} = 110.98\ \mathrm{g\ CaCl_2}$. Dimensional analysis will allow you to calculate the mass of $\mathrm{CaCl_2}$ that you should measure.

$$3.00\ \mathrm{mol\ CaCl_2} \times \frac{110.98\ \mathrm{g\ CaCl_2}}{1\ \mathrm{mol\ CaCl_2}} = 333\ \mathrm{g\ CaCl_2}$$

When you measure the mass of $333\ \mathrm{g}$ of $\mathrm{CaCl_2}$, you are measuring 3.00 moles of $\mathrm{CaCl_2}$.



Figure 6.5.2: Calcium chloride is used as a drying agent and as a road deicer. (Credit: Martin Walker (User:Walkerma/Wikimedia Commons); Source: http://commons.wikimedia.org/wiki/File:Calcium_chloride.jpg(opens in new window); License: Public Domain)

Example 6.5.1: Converting Moles to Mass

Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.

Solution

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

Known

- Molar mass of $\mathrm{Cr} = 52.00\ \mathrm{g/mol}$
- $0.560\ \mathrm{mol\ Cr}$

Unknown

- $0.560\ \text{mol Cr}$ = ? g

One conversion factor will allow us to convert from the moles of Cr to mass.

Step 2: Calculate.

$$0.560\ \text{mol Cr} \times \frac{52.00\ \text{g Cr}}{1\ \text{mol Cr}} = 29.1\ \text{g Cr}$$

Step 3: 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 $0.560\ \text{mol}$.

A similar conversion factor utilizing molar mass can be used to convert from the mass of a substance to moles. In a laboratory situation, you may perform a reaction and produce a certain amount of a product which can be massed. It will often then be necessary to determine the number of moles of the product that was formed. The next problem illustrates this situation.

Example 6.5.2: Converting Mass to Moles

A certain reaction produces $2.81\ \text{g}$ of copper (II) hydroxide, Cu(OH)_2. Determine the number of moles produced in the reaction.

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

Known

- mass = 2.81g

Unknown

- mol Cu(OH)_2

One conversion factor will allow us to convert from mass to moles.

Step 2: Calculate.

First, it is necessary to calculate the molar mass of Cu(OH)_2 from the molar masses of Cu, O, and H. The molar mass is $97.57\ \text{g/mol}$.

$$2.81\ \text{g Cu(OH)}_2 \times \frac{1\ \text{mol Cu(OH)}_2}{97.57\ \text{g Cu(OH)}_2} = 0.0288\ \text{mol Cu(OH)}_2$$

Step 3: Think about your result.

The relatively small mass of product formed results in a small number of moles.



Summary

- Calculations involving conversions between moles of a material and the mass of that material are described.

Review

1. You have 19.7 grams of a material and wonder how many moles were formed. Your friend tells you to multiply the mass by grams/mole. Is your friend correct?
2. How many grams of MgO are in 3.500 moles?
3. How many moles of H_2O are in 15.2 grams of pure ice?

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6.6: Word Equations



Figure **6.6.1** (Credit: User:Daderot/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Innsbruck_-_Schloss_Ambras_-_cookbook_of_Philippine_Welser.jpg(opens in new window); License: Public Domain)

What's for Dinner?

Various ways of recording recipes have developed over the centuries. The cookbook shown above was written by a woman who probably collected all her own recipes. Later, printed cookbooks became available (even guys had no excuse for not being able to cook). Today we can find recipes on a number of internet sites and can quickly search for information on how to cook anything we want. Reading a recipe sometimes requires we understand a few codes and symbols (what's the difference between a tsp and a Tsp?), but the information on what we start with and what we end up with is there.

Writing Chemical Equations

Chemical reactions are occurring all around us. Plants use sunlight to drive their photosynthetic process and produce energy. Cars and other vehicles burn gasoline in order to power their engines. Batteries use electrochemical reactions to produce energy and power many everyday devices. Many chemical reactions are going on within the human body as well, particularly during the digestion of food.

In math class, you have written and solved many mathematical equations. Chemists keep track of chemical reactions by writing equations as well. In any chemical reaction, one or more substances—called **reactants**—are converted into one or more new substances—called **products**. The general form of the equation for such a process looks like this:

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

Unlike a math equation, a chemical equation does not use an equal sign. Instead, the arrow is called a yield sign and so the equation is described as "reactants yield products".

Word Equations

You can describe a chemical reaction by writing a **word equation**. When silver metal is exposed to sulfur, it reacts to form silver sulfide. Silver sulfide is commonly known as tarnish and turns the surface of silver objects dark and streaky black (see figure below). The sulfur that contributes to tarnish can come from traces of sulfur in the air, or from foods such as eggs. The word equation for the process is:

$$\text{Silver} + \text{sulfur} \rightarrow \text{Silver sulfide}$$

The silver and the sulfur are the reactants in the equation, while the silver sulfide is the product.



Figure **6.6.2:** You can see dark spots of tarnished (silver sulfide) forming on this ring as it reacts with sulfur compounds in the air. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Another common chemical reaction is the burning of methane gas. Methane is the major component of natural gas and is commonly burned on a gas stove or in a Bunsen burner (figure below). Burning is a chemical reaction in which some type of fuel is reacted with oxygen gas. The products of the reaction in the burning of methane, as well as other fuels, are carbon dioxide and water. The word equation for this reaction is:

$$\text{Methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

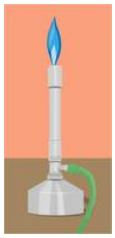


Figure **6.6.3**: A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Word equations can be very useful, but do have one major drawback—they cannot be used for any quantitative work. A word equation does not tell how many moles of each material are needed, or how many moles of product are formed.



Summary

- Word equations are used to describe the conversion of reactants to products.

Review

1. Write the generic form of a chemical reaction.
2. What are reactants?
3. What are products?

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6.7: Chemical Equations



Figure 6.7.1 (Credit: jons2 at pdphoto.org; Source: http://commons.wikimedia.org/wiki/File:Shrimp_gumbo.jpg(opens in new window); License: Public Domain)

How do you make shrimp gumbo?

Shrimp gumbo is one of many dishes that are part of the Cajun culture in Louisiana. It's a spicy dish that needs careful control of all the ingredients so that it has a "kick", but is not overwhelming. Recipes convey not only what the preparation entails, but also describe how much of each ingredient is needed, and the details of how to cook the meal. Similarly, we need this type of information in order to carry out chemical reactions successfully and safely.

Chemical Equations

Word equations are time-consuming to write and do not prove to be convenient for many of the things that chemists need to do with equations. A **chemical equation** is a representation of a chemical reaction that displays the reactants and products with chemical formulas. The chemical equation for the reaction of methane with oxygen is shown:

$$\mathrm{CH_4 + O_2 \rightarrow CO_2 + H_2O}$$

The equation above, called a **skeleton equation**, is an equation that shows only the formulas of the reactants and products with nothing to indicate the relative amounts. The first step in writing an accurate chemical equation is to write the skeleton equation, making sure that the formulas of all substances involved are written correctly. All reactants are written to the left of the yield arrow, separated from one another by a plus sign. Likewise, products are written to the right of the yield arrow, also separated with a plus sign.

It is often important to know the physical states of the reactants and products taking part in a reaction. To do this, put the appropriate symbol in parentheses after each formula: (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous (water-based) solution. The previous reaction becomes:

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

The table below shows a listing of symbols used in chemical equations. Some, such as the double arrow which represents equilibrium, and the use of a catalyst in a reaction, will be detailed in other concepts.

Table 6.7.1: Symbols Used in Chemical Equations

Symbols	Description
$+$	Used to separate multiple reactants or products.
$\rightarrow$	Yield sign; separates reactants from products.
$\rightleftharpoons$	Replaces the yield sign for reversible reactions that reach equilibrium.
(s)	Reactant or product in the solid state.
(l)	Reactant or product in the liquid state.
(g)	Reactant or product in the gaseous state.
(aq)	Reactant or product in an aqueous solution (dissolved in water).
$\xrightarrow{\text{Pt}}$	Formula written above the arrow is used as a catalyst in the reaction.
$\xrightarrow{\Delta}$	Triangle indicates that the reaction is being heated.



Summary

- A chemical equation is representation a chemical reaction using chemical formulas reactants and products, as well as symbols.
- Symbols used in chemical equations are described and explained.

Review

1. What does a skeleton equation tell you?
2. Why would you want to know the physical state of materials in a chemical reaction?
3. In a chemical reaction what does symbol → mean?
4. If I see Δ over the arrow, what does this indicate?

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6.8: Balancing Equations



Figure **6.8.1** (Credit: Joseph Allen; Source: http://commons.wikimedia.org/wiki/File:John_Dalton.jpeg(opens in new window); License: Public Domain)

Any leftovers?

When you cook a meal, quite often there are leftovers because you prepared more than people would eat at one sitting. Sometimes when you repair a piece of equipment, you end up with what are called "pocket parts"—small pieces you put in your pocket because you're not sure where they belong. Chemistry tries to avoid leftovers and pocket parts. In normal chemical processes, we cannot create or destroy matter (law of conservation of mass). If we start out with ten carbon atoms, we need to end up with ten carbon atoms. John Dalton's atomic theory said that chemical reactions basically involve the rearrangement of atoms. Chemical equations need to follow these principles in order to be correct.

Balancing Chemical Equations

A **balanced equation** is a chemical equation in which mass is conserved and there are equal numbers of atoms of each element on both sides of the equation. We can write a chemical equation for the reaction of carbon with hydrogen gas to form methane ($\mathbf{CH_4}$):

$$\underset{\text{2 C atoms}}{\mathbf{C}\,(s)} \quad + \quad \underset{\text{2 H atoms}}{\mathbf{H_2}\,(g)} \quad \rightarrow \quad \underset{\text{1 C atom, 4 H atoms}}{\mathbf{CH_4}\,(g)}$$

In order to write a correct equation, you must first write the correct skeleton equation with the correct chemical formulas. Recall that hydrogen is a diatomic molecule and so is written as $\mathbf{H_2}$.

When we count the number of atoms of both elements, shown under the equation, we see that the equation is not balanced. There are only 2 atoms of hydrogen on the reactant side of the equation, while there are 4 atoms of hydrogen on the product side. We can balance the above equation by adding a coefficient of 2 in front of the formula for hydrogen.

$$\mathbf{C}\,(s) + \mathbf{2H_2}\,(g) \rightarrow \mathbf{CH_4}\,(g)$$

A **coefficient** is a small whole number placed in front of a formula in an equation in order to balance it. The 2 in front of the $\mathbf{H_2}$ means that there are a total of $\mathbf{2 \times 2 = 4}$ atoms of hydrogen as reactants. Visually, the reaction looks like the figure below.

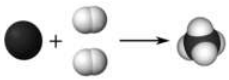


Figure **6.8.2**: Reaction between carbon and hydrogen to form methane. (Credit: Ben Mills (Wikimedia: Benjah-bmm27; Source: http://commons.wikimedia.org/wiki/File:Dihydrogen-3D-vdW.png(opens in new window) and http://commons.wikimedia.org/wiki/File:Methane-3D-space-filling.png(opens in new window); License: Public Domain)

In the balanced equation, there is one atom of carbon and four atoms of hydrogen on both sides of the arrow. Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product.
2. Write the skeleton equation.
3. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
4. Balance each element one at a time by placing coefficients in front of the formulas.
    a. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation.

b. No coefficient is written for a 1.

c. NEVER change the subscripts in a chemical formula—you can only balance equations by using coefficients.

5. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
6. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

Example 6.8.1: Balancing Chemical Equations

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

Step 1: Plan the problem.

Follow the steps for writing and balancing a chemical equation listed in the text.

Step 2: Solve.

Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2\,(aq) + NaCl\,(aq) \rightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$$

Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	1 NO_3^- ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $\mathrm{NaNO_3}$. The result is:

$$\mathrm{Pb(NO_3)_2\,(aq) + 2NaCl\,(aq) \rightarrow 2NaNO_3\,(aq) + PbCl_2\,(s)}$$

The new count for each atom and polyatomic ion becomes:

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	2 NO_3^- ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 3: Think about your result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation.



Summary

- The process of balancing chemical equations is described.

Review

1. What is the law of conservation of mass?
2. How did Dalton describe the process of a chemical reaction?
3. Why don’t we change the subscripts in order to balance an equation?

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6.9: Combination Reactions



Figure **6.9.1** (Credit: Rim: User:Relaxatiallc/Wikimedia Commons; Wheel: Christopher Ziemnowicz; Source: Rim: http://commons.wikimedia.org/wiki/File:Ats_amgpenta.jpg(opens in new window); Wheel: http://commons.wikimedia.org/wiki/File:1975_AACA_AMC_Pacer_X_red-white_wheel.jpg(opens in new window); License: Public Domain)

How useful is a wheel rim?

A wheel rim is not very useful by itself. Driving on the rim can damage it and make for a very rough ride. When the rim is combined with a tire, the product can be put on a car and used for a safe and comfortable ride. The two separate items combine to make something that improves the car ride.

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:

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

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

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

In order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules: $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{F_2}$, $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$.

One sort 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.

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



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.

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

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

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

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



Example 6.9.1: Combination Reactions

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

Step 1: Plan the problem.

Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes K^+, while the oxide ion is O^{2-}.

Step 2: Solve.

The skeleton (unbalanced) equation:

$$K(s) + O_2(g) \rightarrow K_2O(s)$$

The equation is then easily balanced with coefficients.

$$4K(s) + O_2(g) \rightarrow 2K_2O(s)$$

Step 3: Think about your result.

Formulas are correct and the resulting combination reaction is balanced.

? Exercise 6.9.1

Can you build a balanced, combination reaction for the formation of aluminum oxide (Al_2O_3)?

Answer

$4Al + 3O_2 \rightarrow 2Al_2O_3$

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide, according to the equation:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Two compounds may also react to form a more complex compound. A very common example is the reaction of an oxide with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

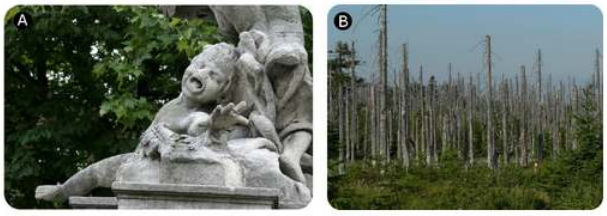


Figure 6.9.2: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain. (Credit: (A) Nipik; (B) Nino Barbieri; Source: (A) http://commons.wikimedia.org/wiki/File:Acid_rain_woods1.JPG(opens in new window); (B) http://commons.wikimedia.org/wiki/File:Pollution_-_Damaged_by_acid_rain.jpg(opens in new window); License: (A) Public Domain; (B) CC by 2.5(opens in new window))

Summary

- Combination reactions occur when two or more substances combine to form a new substance.

Review

1. What are combination reactions?
2. Write the product of the following reaction: $Mg + H_2O \rightarrow$

3. Is $CH_4+2O_2 \rightarrow CO_2+2H_2O$ a combination reaction? Explain your answer.

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6.10: Decomposition Reactions

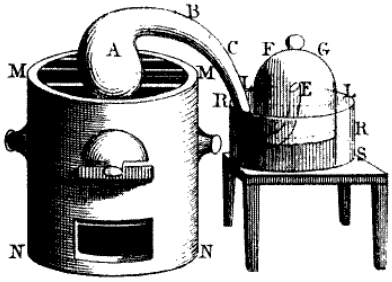


Figure **6.10.1** (Credit: Madame Lavoisier, modified by User: Cdang/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Lavoisier_decomposition_air.png(opens in new window); License: Public Domain)

How does a decomposition reaction work?

Antoine Lavoisier is widely known as the "father of modern chemistry." He was one of the first to study chemical reactions in detail. Lavoisier reacted mercury with oxygen to form mercuric oxide as part of his studies on the composition of the atmosphere. He was then able to show that the decomposition of mercuric oxide produced mercury and oxygen. The diagram above shows the apparatus used by Lavoisier to study the formation and decomposition of mercuric oxide.

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:

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

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.

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



Figure **6.10.2**: *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.* (Credit: Ben Mills (User:Benjah-bmm27/Wikimedia Commons); Source: http://commons.wikimedia.org/wiki/File:Mercury%2528II%2529-oxide.jpg(opens in new window); License: Public Domain)

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:

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

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

$$2\mathrm{NaOH}\,(s) \rightarrow \mathrm{Na_2O}\,(s) + \mathrm{H_2O}\,(g)$$

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

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$$



? Exercise 6.10.1

Can you build a balanced Chemical reaction for the decomposition of Potassium chlorate ($KClO_3$)?

Answer

$2KClO_3 \rightarrow 2KCl + 3O_2$

Example 6.10.1: Decomposition Reactions

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Solution

Step 1: 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.

Step 2: Solve.

The skeleton (unbalanced) equation:

$$H_2O\,(l) \overset{\text{elec}}{\rightarrow} H_2\,(g) + O_2\,(g)$$

Note the abbreviation "**elec**" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation.

$$2H_2O\,(l) \overset{\text{elec}}{\rightarrow} 2H_2\,(g) + O_2\,(g)$$

Step 3: Think about your result.

The products are elements and the equation is balanced.



Summary

- A definition of decomposition reaction and example reactions are given.

Review

1. What is a decomposition reaction?
2. What is usually needed for a decomposition reaction to take place?
3. Are elements always the product of a decomposition reaction?

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6.11: Combustion Reactions



Figure 6.11.1 (Credit: Nina Hale; Source: http://commons.wikimedia.org/wiki/File:RoastingMarshmallow.jpg(opens in new window); License: CC by 2.0(opens in new window))

How do you cook the perfect marshmallow?

Roasting marshmallows over an open fire is a favorite past-time for campers, outdoor cook-outs, and just gathering around a fire in the back yard. The trick is to get the marshmallow a nice golden brown without catching it on fire. Too often we are not successful and we see the marshmallow burning on the stick – a combustion reaction taking place right in front of us.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve $\mathbf{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor:

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

Notice that this reaction also qualifies as a combination reaction.

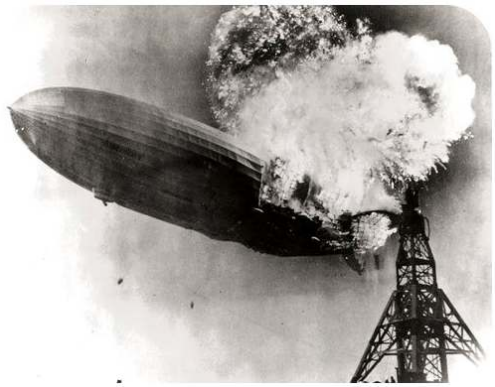


Figure 6.11.2: Explosion of the Hindenberg. (Credit: Courtesy of Gus Pasquerella/US Navy; Source: http://commons.wikimedia.org/wiki/File:Hindenburg_burning.jpg(opens in new window); License: Public Domain)

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.

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane ($\mathbf{C_3H_8}$) is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathbf{C_3H_8}\,(g) + \mathbf{5O_2}\,(g) \rightarrow \mathbf{3CO_2}\,(g) + \mathbf{4H_2O}\,(g)$$

Example 6.11.1: Combustion Reactions

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

Step 1: Plan the problem.

Ethanol and oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.

Step 2: Solve.

Write the skeleton equation:

$$C_2H_5OH\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)$$

Balance the equation.

$$C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(g)$$

Step 3: 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.



Summary

- Combustion reaction is defined and examples are given.

Review

1. What is needed for a combustion reaction to take place?
2. What is formed in any combustion reaction?
3. Mercury reacts with oxygen to form mercuric oxide. Is this a combustion reaction?
4. What are the products of any combustion reaction involving a hydrocarbon?

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6.12: Single Replacement Reactions



Figure 6.12.1 (Credit: wisteriax; Source: https://pixabay.com/photos/still-life-silver-poppies-2312788/(opens in new window); License: Pixabay License)

Why is the silver dark?

The platter and pitcher shown above provides an example of tarnish, a chemical reaction caued when silver metal reacts with hydrogen sulfide gas produced by some industrial processes or as a result of decaying animal or plant materials:

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$

The tarnish can be removed using a number of polishes, but the process also removes a small amount of silver along with the tarnish.

Single-Replacement Reactions

A **single-replacement reaction** is a reaction in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element A is a metal and replaces element B (also a metal) in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$Y + XZ \rightarrow XY + Z$$

(Where Y is a nonmetal and replaces the nonmetal Z in the compound with X.)

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

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

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).

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

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal.



Figure **6.12.2**: Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Credit: User: Chemicalinterest/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Zn_reaction_with_HCl.JPG(opens in new window); License: Public Domain)

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).

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



Figure **6.12.3**: 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. (Credit: User:Ajhalls/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Large_Sodium_Explosion.jpg(opens in new window); License: Public Domain)

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

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

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.



Summary

- The activity series describes the relative reactivities of metals and halogens.

Review

1. What is a metal replacement reaction?
2. Will a non-metal replace a metal?
3. What is the most reactive halogen?
4. What products will I get if I add potassium metal to water?

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6.13: Activity Series



Figure **6.13.1**: Copy and Paste Caption here. (Credit: Sodium: User: Ajhalls/Wikimedia Commons; Silver: User:Daderot/Wikimedia Commons; Source: Sodium: http://commons.wikimedia.org/wiki/File:Large_Sodium_Explosion.jpg(opens in new window); Silver: http://commons.wikimedia.org/wiki/File:Camp_cup_and_tumbler,_1795-1800,_Paul_Revere_silver_collection,_Worcester_Art_Museum_-_IMG_7624.JPG(opens in new window); License: Public Domain)

What's the difference between the two pictures above?

We see above two metals 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. Both metals have a single s electron in their outer shell, so you would predict similar reactivities. However, we have a better tool that allows us to make better prediction about what will react with what.

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 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 **6.13.1**: Activity Series

Activity of Metals		Activity of Halogens
Elements	**Reaction Occurring**	**Elements**
Li **K** **Ba** **Sr** **Ca** **Na**	React with cold water, replacing hydrogen.	$\mathbf{F_2}$ $\mathbf{Cl_2}$ $\mathbf{Br_2}$ $\mathbf{I_2}$
Mg **Al** **Zn** **Cr** **Fe** **Cd**	React with steam, but not cold water, replacing hydrogen.	
Co **Ni** **Sn** **Pb**	Do not react with water. React with acids, replacing hydrogen.	
$\mathbf{H_2}$		
Cu **Hg** **Ag** **Pt** **Au**	Unreactive with water or acids.	

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 6.13.1: Single-Replacement Reactions

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. $\mathrm{Al}\,(s) + \mathrm{Zn(NO_3)_2}\,(aq) \rightarrow$
b. $\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow$

Solution

Step 1: Plan the problem.

For A, compare the placements of aluminum and zinc on the activity series. For B, compare the placements of silver and hydrogen.

Step 2: 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:

$$2\mathrm{Al}\,(s) + 3\mathrm{Zn(NO_3)_2}\,(aq) \rightarrow 2\mathrm{Al(NO_3)_3}\,(aq) + 3\mathrm{Zn}\,(s)$$

Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid.

$$\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow \mathrm{NR}$$



Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the series.

Review

1. What does the activity series tell us?
2. Can a metal undergo any of the reactions listed below it in the series?
3. List two metals that cobalt will displace and two that will displace it.

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6.14: Double Replacement Reactions



Figure **6.14.1** (Credit: F. S. Church, published in Harper's Weekly, January 17, 1874, p. 61; Source: http://commons.wikimedia.org/wiki/File:Barter-Chickens_for_Subscription.jpg(opens in new window); License: Public Domain)

Want to trade?

The practice of barter (trading one thing for another) has been in existence for a very long time. In the illustration above, items like chickens were bartered for newspapers. You have something I want, and I have something you want. So we trade and we each have something new. Some chemical reactions are like that. Compounds swap parts and you have new materials.

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:

$$\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AD} + \mathrm{CB}$$

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:

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s)$$

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



Figure **6.14.2**: Formation of lead iodide precipitate. (Credit: Paige Powers - "Lead Iodide"; Source: https://www.flickr.com/photos/44200742@N07/5533819494(opens in new window); License: CC-BY 2.0)

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 6.14.1: Double-Replacement Reactions

Write a complete and balanced chemical equation for the following double-replacement reactions. One product is indicated as a guide.

a. $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed)
b. $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms)

Solution

Step 1: Plan the problem.

In A, the production of a gas drives the reaction. In B, the production of a precipitate drives the reaction. In both cases, use the ionic charges of both reactants to construct the correct formulas of the products.

Step 2: Solve.

A. The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is:

$$\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$$

B. Ammonium ion and nitrate ion are $1+$ and $1-$ respectively, while barium and sulfate are $2+$ and $2-$. This must be taken into account when exchanging partners and writing the new formulas. Then, the equation is balanced.

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Step 3: Think about your result.

Both are double replacement reactions. All formulas are correct and the equations are balanced.

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.

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



Summary

- The double-replacement reaction generally takes the form of AB + CD → AD + CB where A and C are positively-charged cations, while B and D are negatively-charged anions.
- In a double replacement reactions, typically one of the products is a precipitate, a gas, or a molecular compound.

Review

1. In a double-replacement reaction, what type of compounds are usually the reactants? A double-replacement reaction occurs between sodium sulfide and hydrogen chloride. Write the rest of the chemical equation and balance it.
2. $Na_2S + HCl \rightarrow$
3. In double-replacement reaction, one of three possible types of products usually form. What are the three types?

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6.15: Oxidation-Reduction (Redox) Reactions

Learning Objectives

- To identify a chemical reaction as an oxidation-reduction reaction.

When zinc metal is submerged into a quantity of aqueous **HCl**, the following reaction occurs (Figure **6.15.1**):

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl_2\,(aq)} \tag{6.15.1}$$

This is one example of what is sometimes called a *single replacement reaction* because **Zn** replaces **H** in combination with **Cl**.



Figure **6.15.1**: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 6.15.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \longrightarrow H_2\,(g) + Zn^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the **reducing agent**, and the species being reduced is called the **oxidizing agent**.

> *Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.*

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)}$$

zinc atoms are oxidized to Zn^{2+}. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance:

the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced **reduction half reaction** is as follows:

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$\begin{aligned} &Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ &\underline{2H^+ + \cancel{2e^-} \rightarrow H_2} \\ &Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{aligned}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel**. The following example demonstrates this process.

Example 6.15.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Solution

We start by using symbols of the elements and ions to represent the reaction:

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

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

Reduction half-reaction:

$$Ag^+ + e^- \longrightarrow Ag$$

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

Oxidation half-reaction:

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

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

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

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

- The **substance oxidized** is the reactant that had undergone oxidation: Al
- The **substance reduced** is the reactant that had undergone reduction: Ag^+

- The **reducing agent** is the same as the substance oxidized: Al
- The **oxidizing agent** is the same as the substance reduced: Ag^+

Exercise 6.15.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Answer

Reduction: $Ca^{2+} + 2e^- \rightarrow Ca$

Oxidation: $2\,(K \rightarrow K^+ + e^-)$

Combined: $Ca^{2+} + 2K \rightarrow Ca + 2K^+$

- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: Ca^{2+}
- The **reducing agent** is the same as the substance oxidized: K
- The **oxidizing agent** is the same as the substance reduced: Ca^{2+}

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathrm{Cd\,(s) + 2\,NiOOH\,(s) + 2\,H_2O(\ell) \longrightarrow Cd(OH)_2\,(s) + 2\,Ni(OH)\;2\,(s)}$$

The cadmium is oxidized, while the nickel atoms in NiOOH are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathrm{2\,Li\,(s) + I_2\,(s) \longrightarrow 2\,LiI\,(s)}$$

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.



Figure 6.15.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of **oxidation** was "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule **loses oxygen** atoms, the molecule is being reduced. For example, the acetaldehyde (CH_3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

Table shows how each process affects the change in oxygen and change in hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

Example 6.15.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \rightarrow NH_3$
b. $CH_3CH_2OHCH_3 \rightarrow CH_3COCH_3$
c. HCHO → HCOOH

Solution

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Exercise 6.15.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \rightarrow CO_2 + H_2O$
b. $NO_2 \rightarrow N_2$
c. $CH_2{=}CH_2 \rightarrow CH_3CH_3$

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as

separate chemical equations.

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6.16: Redox Reactions in Organic Chemistry and Biochemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure **6.16.1**: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. from Wikipedia.

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure **6.16.1**).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{6.16.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($\mathrm{C_6H_{12}O_6}$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{6.16.2}$$

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\mathrm{K_2Cr_2O_7}$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal *carbonyl group* (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol ($\mathrm{CH_3CH_2OH}$) in a person's breath:

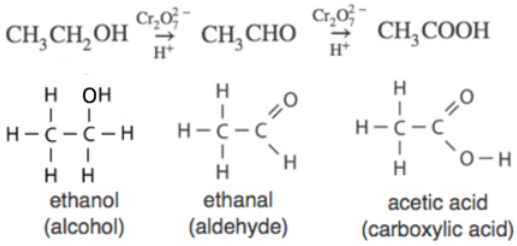
$$\mathrm{3\,CH_3CH_2OH + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O} \tag{6.16.3}$$

If the product acetaldehyde ($\mathrm{CH_3CHO}$) is not removed as it forms, it is further oxidized to acetic acid ($\mathrm{CH_3COOH}$). In this case, the overall reaction is as follows:

$$\mathrm{3\,CH_3CH_2OH + 2\,Cr_2O_7^{2-} + 16\,H^+ \rightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11\,H_2O} \tag{6.16.4}$$

In this reaction, the chromium atom is reduced because it lost oxygen atoms from $Cr_2O_7^{2-}$ to Cr^{3+}. On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol (CH_3CH_2OH, a.k.a. ethanol) to form acetaldehayde (CH_3CHO, a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.



When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol ($\mathbf{CH_3CHOHCH_3}$). It is the common solvent acetone [$\mathbf{(CH_3)_2CO}$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$\mathbf{3\,CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,(CH_3)_2CO + 2\,Cr^{3+} + 7\,H_2O} \tag{6.16.5}$$

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($\mathbf{CH_3COCOOH}$) is reduced to lactic acid ($\mathbf{CH_3CHOHCOOH}$) in the muscles.

$$\mathbf{CH_3COCOOH \rightarrow CH_3CHOHCOOH} \tag{6.16.6}$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $\mathbf{C_6H_8O_6}$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($\mathbf{C_6H_6O_6}$). In the stomach, ascorbic acid reduces the nitrite ion ($\mathbf{NO_2^-}$) to nitric oxide ($\mathbf{NO}$):

$$\mathbf{C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO} \tag{6.16.7}$$

> *If reaction in Equation 6.16.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure **6.16.2**).



Figure **6.16.2**: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($\mathbf{C_6H_{12}O_6}$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure **6.16.3**). The overall change that occurs is as follows:

$$\mathbf{6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2} \tag{6.16.8}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure **6.16.3**: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

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6.17: Quantitative Relationships Based on Chemical Equations

Learning Objectives

- To calculate the amount of one substance that will react with or be produced from a given amount of another substance.

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made.

> *The word stoichiometry is pronounced "stow-eh-key-OM-et-tree." It is of mixed Greek and English origins, meaning roughly "measure of an element."*

Looking Closer: Stoichiometry in Cooking

Let us consider a stoichiometry analogy from the kitchen. A recipe that makes 1 dozen biscuits needs 2 cups of flour, 1 egg, 4 tablespoons of shortening, 1 teaspoon of salt, 1 teaspoon of baking soda, and 1 cup of milk. If we were to write this as a chemical equation, we would write

$$\text{2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk} \rightarrow \text{12 biscuits}$$

(Unlike true chemical reactions, this one has all 1 coefficients written explicitly—partly because of the many different units here.) This equation gives us ratios of how much of what reactants are needed to make how much of what product. Two cups of flour, when combined with the proper amounts of the other ingredients, will yield 12 biscuits. One teaspoon of baking soda (when also combined with the right amounts of the other ingredients) will make 12 biscuits. One egg must be combined with 1 cup of milk to yield the product food. Other relationships can also be expressed.

We can use the ratios we derive from the equation for predictive purposes. For instance, if we have 4 cups of flour, how many biscuits can we make if we have enough of the other ingredients? It should be apparent that we can make a double recipe of 24 biscuits.

But how would we find this answer formally, that is, mathematically? We would set up a conversion factor, much like we did in Chapter 1. Because 2 cups of flour make 12 biscuits, we can set up an equivalency ratio:

$$\frac{\text{12 biscuits}}{\text{2 c flour}}$$

We then can use this ratio in a formal conversion of flour to biscuits:

$$\text{4 c flour} \times \frac{\text{12 biscuits}}{\text{2 c flour}} = \text{24 biscuits}$$

Similarly, by constructing similar ratios, we can determine how many biscuits we can make from any amount of ingredient. When you are doubling or halving a recipe, you are doing a type of stoichiometry. Applying these ideas to chemical reactions should not be difficult if you use recipes when you cook.



A recipe shows how much of each ingredient is needed for the proper reaction to take place. from Wikipedia.

Consider the following balanced chemical equation:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \tag{6.17.1}$$

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Table uses a statement from the balanced chemical reaction to show ratios and inverse ratios.

Statement from the Balanced Chemical Reaction	Ratio	Inverse Ratio
two C_2H_2 molecules react with five O_2 molecules	$\frac{2C_2H_2}{5O_2}$	$\frac{5O_2}{2C_2H_2}$
two C_2H_2 molecules react to make four CO_2 molecules	$\frac{2C_2H_2}{4CO_2}$	$\frac{4CO_2}{2C_2H_2}$
five O_2 molecules react to make two H_2O molecules	$\frac{5O_2}{2H_2O}$	$\frac{2H_2O}{5O_2}$
four CO_2 molecules are made at the same time as two H_2O molecules	$\frac{2H_2O}{4CO_2}$	$\frac{4CO_2}{2H_2O}$

Other relationships are possible; in fact, 12 different conversion factors can be constructed from this balanced chemical equation. In each ratio, the unit is assumed to be molecules because that is how we are interpreting the chemical equation.

Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO_2 molecules are formed when 26 molecules of C_2H_2 are reacted. As usual with a conversion problem, we start with the amount we are given—$26C_2H_2$—and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO_2. That conversion factor is $\frac{4CO_2}{2C_2H_2}$, which is composed of terms that come directly from the balanced chemical equation. Thus, we have

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2}$$

The molecules of C_2H_2 cancel, and we are left with molecules of CO_2. Multiplying through, we get

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2} = 52CO_2$$

Thus, 52 molecules of CO_2 are formed.

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.

Example 6.17.1

Start with this balanced chemical equation.

$$\mathrm{KMnO_4 + 8\,HCl + 5\,FeCl_2 \longrightarrow 5\,FeCl_3 + MnCl_2 + 4\,H_2O + KCl}$$

1. Verify that the equation is indeed balanced.
2. Give 2 ratios that give the relationship between HCl and $FeCl_3$.

Solution

1. Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H_2O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 $FeCl_2$ reactants and 5 $FeCl_3$ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 $FeCl_2$ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 $FeCl_3$ formula units, 2 from the $MnCl_2$ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.
2. Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 $FeCl_3$ formula units, we have the following 2 ratios: $\frac{\mathrm{8\,HCl}}{\mathrm{5\,FeCl_3}}$ and $\frac{\mathrm{5\,FeCl_3}}{\mathrm{8\,HCl}}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

Exercise 6.17.1

Start with this balanced chemical equation.

$$\mathrm{2KMnO_4 + 3CH_2{=}CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2CH_2OH + 2KOH}$$

a. Verify that the equation is balanced.
b. Give 2 ratios that give the relationship between $KMnO_4$ and $CH_2{=}CH_2$. (A total of 30 relationships can be constructed from this chemical equation. Can you find the other 28?)

Answer a:

Each side has 2 K atoms and 2 Mn atoms. On the reactant side, 3 $CH_2{=}CH_2$ yield 6 C atoms and on the product side, 3 $HOCH_2CH_2OH$ also yield 6 C atoms, so the C atoms are balanced. There are 20 H atoms on the reactants side: 12 H atoms from 3 $CH_2{=}CH_2$ and 8 H atoms from 4 H_2O. On the product side, there are also 20 H atoms: 18 H atoms from 3 $HOCH_2CH_2OH$ and 2 H atoms from 2 KOH. So, the H atoms are balanced. As for O, on the reactant side, there are 8 O atoms from 2 $KMnO_4$ and 4 O atoms from 4 H_2O, for a total of 12 O atoms. On the product side, there are 4 O atoms from the 2 MnO_2 formula units, 6 O atoms from 3 $HOCH_2CH_2OH$, and 2 O atoms from the 2 KOH formula units. This is a total of 12 O atoms in the products, so the O atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Answer b:

Because the balanced chemical equation tells us that 2 $KMnO_4$ formula units react with 3 $CH_2{=}CH_2$ molecules, we have the following 2 ratios: $\frac{\mathrm{2KMnO_4}}{\mathrm{3CH_2{=}CH_2}}$ and $\frac{\mathrm{3CH_2{=}CH_2}}{\mathrm{2KMnO_4}}$. There are a total of 30 possible ratios. Can you find the other 28 relationships?

Key Takeaway

The coefficients in a balanced chemical equation give the ratios in which molecules of substances react and are produced in a chemical reaction.

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6.18: Mass-Mole Stoichiometry



Figure **6.18.1** (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Need nails?

When you are doing a large construction project, you have a good idea of how many nails you will need (lots!). When you go to the hardware store, you don't want to sit there and count out several hundred nails. You can buy nails by weight, so you determine how many nails are in a pound, calculate how many pounds you need, and you're on your way to begin building.

While the mole ratio is ever-present in all stoichiometry calculations, amounts of substances in the laboratory are most often measured by mass. Therefore, we need to use mole-mass calculations in combination with mole ratios to solve several different types of mass-based stoichiometry problems.

Mass to Moles Problems

In this type of problem, the mass of one substance is given, usually in grams. From this, you are to determine the amount in moles of another substance that will either react with or be produced from the given substance.

$$\textbf{mass of given} \rightarrow \textbf{moles of given} \rightarrow \textbf{moles of unknown}$$

The mass of the given substance is converted into moles by use of the molar mass of that substance from the periodic table. Then, the moles of the given substance are converted into moles of the unknown by using the mole ratio from the balanced chemical equation.

Example 6.18.1: Mass-Mole Stoichiometry

Tin metal reacts with hydrogen fluoride to produce tin (II) fluoride and hydrogen gas, according to the following balanced equation.

$$\mathrm{Sn}\,(s) + 2\mathrm{HF}\,(g) \rightarrow \mathrm{SnF_2}\,(s) + \mathrm{H_2}\,(g)$$

How many moles of hydrogen fluoride are required to react completely with $75.0\ \mathrm{g}$ of tin?

Solution:

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

Known

- Given: $75.0\ \mathrm{g\ Sn}$
- Molar mass of $\mathrm{Sn} = 118.69\ \mathrm{g/mol}$
- $1\ \mathrm{mol\ Sn} = 2\ \mathrm{mol\ HF}$ (mole ratio)

Unknown

- mol HF

Use the molar mass of Sn to convert the grams of Sn to moles. Then use the mole ratio to convert from $\mathrm{mol\ Sn}$ to $\mathrm{mol\ HF}$. This will be done in a single two-step calculation.

$\mathrm{g\ Sn} \rightarrow \mathrm{mol\ Sm} \rightarrow \mathrm{mol\ HF}$

Step 2: Solve.

$$75.0\ \mathrm{g\ Sn} \times \frac{1\ \mathrm{mol\ Sn}}{118.69\ \mathrm{g\ Sn}} \times \frac{2\ \mathrm{mol\ HF}}{1\ \mathrm{mol\ Sn}} = 1.26\ \mathrm{mol\ HF}$$

Step 3: Think about your result.

The mass of tin is less than one mole, but the 1:2 ratio means that more than one mole of **HF** is required for the reaction. The answer has three significant figures because the given mass has three significant figures.

Moles to Mass Problems

In this type of problem, the amount of one substance is given in moles. From this, you are to determine the mass of another substance that will either react with or be produced from the given substance.

$$\textbf{moles of given} \rightarrow \textbf{moles of unknown} \rightarrow \textbf{mass of unknown}$$

The moles of the given substance are first converted into moles of the unknown by using the mole ratio from the balanced chemical equation. Then, the moles of the unknown are converted into mass in grams by use of the molar mass of that substance from the periodic table.

Example 6.18.2: Mole-Mass Stoichiometry

Hydrogen sulfide gas burns in oxygen to produce sulfur dioxide and water vapor:

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

What mass of oxygen gas is consumed in a reaction that produces $4.60\ \text{mol}\ SO_2$?

Solution:

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

Known

- Given: $4.60\ \text{mol}\ SO_2$
- $2\ \text{mol}\ SO_2 = 3\ \text{mol}\ O_2$ (mole ratio)
- Molar mass of $O_2 = 32.00\ \text{g/mol}$

Unknown

- mass O_2 = ? g

Use the mole ratio to convert from $\text{mol}\ SO_2$ to $\text{mol}\ O_2$. Then convert $\text{mol}\ O_2$ to grams. This will be done in a single two-step calculation.

$\text{mol}\ SO_2 \rightarrow \text{mol}\ O_2 \rightarrow \text{g}\ O_2$

Step 2: Solve.

$$4.60\ \text{mol}\ SO_2 \times \frac{3\ \text{mol}\ O_2}{2\ \text{mol}\ SO_2} \times \frac{32.00\ \text{g}\ O_2}{1\ \text{mol}\ O_2} = 221\ \text{g}\ O_2$$

Step 3: Think about your result.

According to the mole ratio, $6.90\ \text{mol}\ O_2$ is produced with a mass of $221\ \text{g}$. The answer has three significant figures because the given number of moles has three significant figures.



Summary

- Calculations involving conversions of mass to moles and moles to mass are described.

Review

1. In the first problem, what would happen if you multiply grams Sn by 118.69 grams/mole Sn?
2. Why is a balanced equation needed?
3. Does the physical form of the material matter for these calculations?

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6.19: Mass-Mass Stoichiometry



Figure 6.19.1 (Credit: Pauline Mak; Source: http://www.flickr.com/photos/__my__photos/5591677002/(opens in new window); License: CC by 2.0(opens in new window))

How many walnuts are needed to equal 250 grams?

I want to send 250 grams of shelled walnuts to a friend (don't ask why- just go with the question). How many walnuts in shells do I need to buy? To figure this out, I need to know how much the shell of a walnut weighs (about 40% of the total weight of the unshelled walnut). I can then calculate the mass of walnuts that will yield 250 grams of shelled walnuts, and then determine how many walnuts I need to buy.

Mass to Mass Problems

Mass-mass calculations are the most practical of all mass-based stoichiometry problems. Moles cannot be measured directly, while the mass of any substance can generally be easily measured in the lab. This type of problem is three steps, and is a combination of the two previous types.

$$\text{mass of given} \rightarrow \text{moles of given} \rightarrow \text{moles of unknown} \rightarrow \text{mass of unknown}$$

The mass of the given substance is converted into moles by use of the molar mass of that substance from the periodic table. Then, the moles of the given substance are converted into moles of the unknown by using the mole ratio from the balanced chemical equation. Finally, the moles of the unknown are converted to mass by use of its molar mass.

Example 6.19.1: Mass-Mass Stoichiometry

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

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

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

Solution

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

Known

- Given: $45.7\ g\ NH_4NO_3$
- $1\ mol\ NH_4NO_3 = 1\ mol\ N_2O = 2\ mol\ H_2O$
- Molar mass of $NH_4NO_3 = 80.06\ g/mol$
- Molar mass of $N_2O = 44.02\ g/mol$
- Molar mass of $H_2O = 18.02\ g/mol$

Unknown

- Mass $N_2O = ?\ g$
- Mass $H_2O = ?\ g$

Perform two separate three-step mass-mass calculations, as shown below.

$$g\ NH_4NO_3 \rightarrow mol\ NH_4NO_3 \rightarrow mol\ N_2O \rightarrow g\ N_2O$$

$$g\ NH_4NO_3 \rightarrow mol\ NH_4NO_3 \rightarrow mol\ H_2O \rightarrow g\ H_2O$$

Step 2: Solve.

$$45.7\ \text{g}\ \text{NH}_4\text{NO}_3 \times \frac{1\ \text{mol}\ \text{NH}_4\text{NO}_3}{80.06\ \text{g}\ \text{NH}_4\text{NO}_3} \times \frac{1\ \text{mol}\ \text{N}_2\text{O}}{1\ \text{mol}\ \text{NH}_4\text{NO}_3} \times \frac{44.02\ \text{g}\ \text{N}_2\text{O}}{1\ \text{mol}\ \text{N}_2\text{O}} = 25.1\ \text{g}\ \text{N}_2\text{O}$$

$$45.7\ \text{g}\ \text{NH}_4\text{NO}_3 \times \frac{1\ \text{mol}\ \text{NH}_4\text{NO}_3}{80.06\ \text{g}\ \text{NH}_4\text{NO}_3} \times \frac{2\ \text{H}_2\text{O}}{1\ \text{mol}\ \text{NH}_4\text{NO}_3} \times \frac{18.02\ \text{g}\ \text{H}_2\text{O}}{1\ \text{mol}\ \text{H}_2\text{O}} = 20.6\ \text{g}\ \text{H}_2\text{O}$$

Step 3: 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.



Summary

- Mass-mass calculations involve converting the mass of a reactant to moles of reactant, then using mole ratios to determine moles of product which can then be converted to mass of product.

Review

1. If matter is neither created nor destroyed, why can't we just go directly from grams of reactant to grams of product?
2. Why is it important to get the subscripts correct in the formulas?
3. Why do the coefficients need to be correct?

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6.20: Energy and Chemical Bonds

Learning Objectives

- Define energy and distinguish the different types of energy, potential and kinetic.

Chemical changes and their accompanying changes in *energy* are important parts of our everyday world (Figure **6.20.1**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a) (b) (c)

Figure **6.20.1**: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, often referred to as *stored energy*, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure **6.20.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **6.20.2**: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. **Heat** is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

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6.21: Heat Changes during Chemical Reactions

Learning Objectives

- Define *bond dissociation energy*.
- Determine if a chemical process is exothermic or endothermic.

A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

Bond Dissociation Energy

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process by putting energy into a molecule, which causes its bonds to break, separating the molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the **bond dissociation energy**, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term bond dissociation energy is usually used to describe the *strength* of interactions between atoms that make covalent bonds. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. The C=C bond is stronger than C-C (as discussed in relation to bond length in Section 4.4). For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond dissociation energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond dissociation energy of a C–H bond as being about 100 kcal/mol. Table **6.21.1** lists the approximate bond dissociation energies of various covalent bonds.

Table **6.21.1**: Approximate Bond Dissociation Energies

Bond	Bond Dissociation Energy (kcal/mol)
C–H	100
C–O	86
C=O	190
C–N	70
C–C	85
C=C	145
C≡C	200
N–H	93
H–H	105
Br-Br	46
Cl–Cl	58
O–H	110
O=O	119
H–Br	87
H–Cl	103

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The energy change, for a given reaction can be calculated using the bond dissociation energy values from Table **6.21.1**.

Enthalpy Change or Heat of Reaction, Δ*H*

During a chemical reaction, bonds are broken and new bonds are formed. Breaking chemical bonds is **endothermic**, a process that requires an input of energy or absorption of heat. The reverse process of bond breaking is bond formation, which is **exothermic**, meaning it releases energy or gives off heat. The bond dissociation energy values listed in the above table give the amount of energy required to break a specific bond. When that same bond is reformed, an identical amount of energy is released. The numerical *value* of energy is the same for breaking and forming a bond, but the sign, or *direction* of the process is different. The overall energy change of a specific bond breaking and reforming would be zero, in other words energy is neither created or destroyed, following the law of conservation of energy.

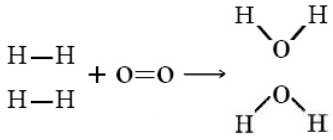
In a chemical reaction, the bonds breaking are often different than the bonds reforming, sometimes there is more heat absorbed (more bonds are broken) and sometimes more heat is released (more bonds are formed). The measured *difference* between the total heat absorbed and the total heat released during a chemical reaction (performed at constant pressure) is called the **heat of reaction** or **enthalpy change**, and is represented by the symbol Δ*H* (where the Δ stands for change and the H represents enthalpy).

$$\begin{aligned}\text{enthalpy change} \approx \Sigma\ &(\text{bond dissociation energies}_{reactants}) \\ -\ \Sigma\ &(\text{bond dissociation energies}_{products})\end{aligned} \tag{6.21.1}$$

The ≈ sign is used because we are adding together *average* bond dissociation energies; hence this approach does not give exact values for the enthalpy change, Δ*H*.

Let's consider the reaction of 2 mols of hydrogen gas (H_2) with 1 mol of oxygen gas (O_2) to give 2 mol water:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \tag{6.21.2}$$



H–H = 105 kcal/mol O=O = 119 kcal/mol O–H = 110 kcal/mol

In this reaction, 2 H–H bonds and 1 O=O bonds from the reactant side are broken, while 4 O–H bonds (two for each H_2O) are formed on the product side. The energy changes can be tabulated and calculated as follows:

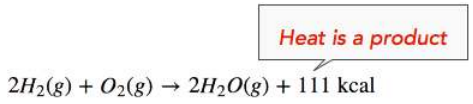
Reactant Bond Dissociation Energy (kcal/mol)		Product Bond Dissociation Energy (kcal/mol)	
2 H–H	2 mol x 105 kcal/mol = 210 kcal	4 O–H	4 mols x 110 kcal/mol = 440 kcal
1 O=O	1 mol x 119 kcal/mol = 119 kcal		
	Total = 329 kcal		**Total** = 440 kcal

$$\Delta H \approx \Sigma \text{ (bond dissociation energies}_{reactants}) - \Sigma \text{ (bond dissociation energies}_{products}) \tag{6.21.3}$$

$$\Delta H \approx 329 \text{ kcal} - 440 \text{ kcal} \tag{6.21.4}$$

$$\Delta H \approx -111 \text{ kcal} \tag{6.21.5}$$

The enthalpy change (ΔH) of the reaction is approximately −111 kcal/mol. This means that bonds in the products (440 kcal) are stronger than the bonds in the reactants (329 kcal) by about 111 kcal/mol. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it absorbs. This excess energy is **released** as heat, so the reaction is **exothermic**. Hence, we can re-write the reaction with the heat released (111 kcal) on the **product side** of the equation, as follows:



We can also re-write the reaction equation with the ΔH information (see below). Note that an **exothermic** reaction has a **negative ΔH** value.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H = -111 \text{ kcal} \tag{6.21.6}$$

Example 6.21.1

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic?

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g) \tag{6.21.7}$$

Solution

Step 1- First look at the equation and identify which bonds exist on in the reactants (bonds broken).

- one H-H bond and
- one Br-Br bond

Step 2- Do the same for the products (bonds formed)

- two H-Br bonds

Step 3- Identify the bond dissociation energies of these bonds from Table **6.21.1**:

- H-H bonds: 105 kcal/mol
- Br-Br bonds: 46 kcal/mol

Step 4- Set up the table (see below) and apply the formula for enthalpy change.

Reactant Bond Dissociation Energy (kcal/mol)		Product Bond Dissociation Energy (kcal/mol)	
1 H–H	1 mol x 105 kcal/mol = 105 kcal	2 H–*Br*	2 mols x 87 kcal/mol = 174 kcal
1 Br–Br	1 mol x 46 kcal/mol = 46 kcal		
	Total = 151 kcal		**Total** = 174 kcal

$$\Delta H \approx 151 \text{ kcal} - 174 \text{ kcal} \tag{6.21.8}$$

$$\Delta H \approx -23 \text{ kcal} \tag{6.21.9}$$

Step 5- Since ΔH is negative (−23 kcal), the reaction is *exothermic*.

Exercise 6.21.1

Using the bond dissociation energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \tag{6.21.10}$$

Is the reaction written above exothermic or endothermic? Explain.

Answer

ΔH = −43 kcal

Since ΔH is negative (−43 kcal), the reaction is *exothermic*.

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6.22: Exothermic and Endothermic Reactions

Learning Objectives

- Use bond dissociation energies to calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. Endothermic reactions *require* energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases (ΔH is positive). As discussed in the previous section, heat is released (considered a product) in an exothermic reaction, and the enthalpy of the system decreases (ΔH is negative).

In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases (gets cold). A chemical reaction is exothermic if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, the temperature of the surroundings increases. See Figure **6.22.1**.

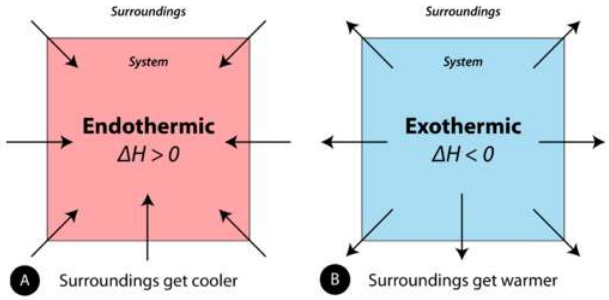


Figure **6.22.1**: (A) Endothermic reaction. (B) Exothermic reaction.

Endothermic Reaction: When 1 **mol** of calcium carbonate decomposes into **1 mol** of calcium oxide and **1 mol** of carbon dioxide, **177.8 kJ** of heat is absorbed. Because the heat is absorbed by the system, the **177.8 kJ** is written as a *reactant*. The ΔH is *positive* for an endothermic reaction.

Heat is a reactant

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

$$\mathrm{CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)} \quad \Delta H = +177.8\ \mathrm{kJ} \tag{6.22.1}$$

Exothermic Reaction: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of **1 mol** of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the product side of the reaction. Another way is to write the ΔH information with a *negative* sign, $-890.4\ \mathrm{kJ}$.

Heat is a product

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

$$\mathrm{CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)} \quad \Delta H = -890.4\ \mathrm{kJ} \tag{6.22.2}$$

Example 6.22.1

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.

b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

? Exercise 6.22.1

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\ (g) + 130\ kcal$

b. $2C(s) + H_2(g) + 5.3\ kcal \rightarrow C_2H_2(g)$

Answer

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in Figure 6.22.2. In endothermic reactions, the reactants have higher bond energy (*stronger bonds*) than the products. Strong bonds have lower potential energy than weak bonds. Hence, the energy of the reactants is lower than that of the products. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure 6.22.2*A*. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the energy of the products is lower than the energy of the reactants, hence is energetically downhill, shown in Figure 6.22.2*B*. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

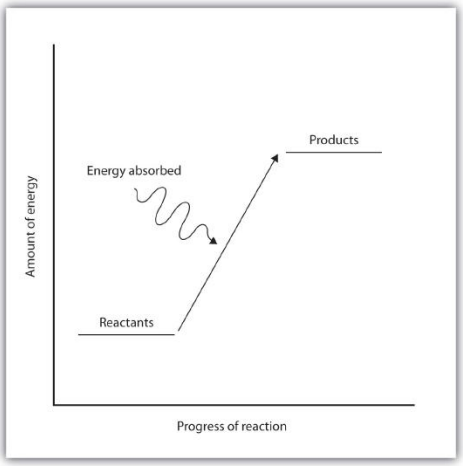


Figure 6.22.2*A*: Endothermic Reactions

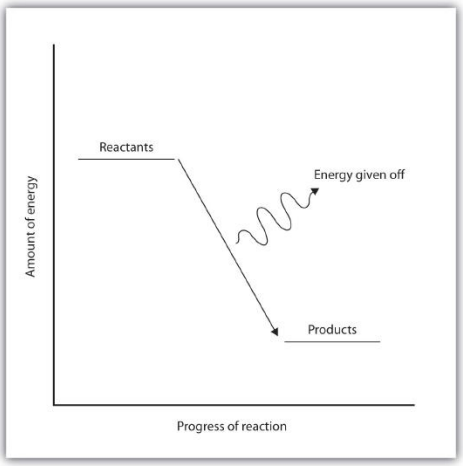


Figure 6.22.2*B*: Exothermic Reactions

Table 6.22.1: Endothermic and Exothermic Reactions

Endothermic Reactions	Exothermic Reactions
Heat is absorbed by reactants to form products.	Heat is released.
Heat is absorbed from the surroundings; as a result, the surroundings get cold.	Heat is released by the reaction to surroundings; surroundings feel hot.
ΔH_{rxn} is positive	ΔH_{rxn} is negative
The bonds broken in the reactants are stronger than the bonds formed in the products.	The bonds formed in the products are stronger than the bonds broken in the reactants.
The reactants are lower in energy than the products.	The products are lower in energy than the reactants.
Represented by an "uphill" energy diagram.	Represented by an "downhill" energy diagram

Concept Review Exercises

1. What is the connection between energy and chemical bonds?
2. Why does energy change during the course of a chemical reaction?
3. Two different reactions are performed in two identical test tubes. In reaction A, the test tube becomes very warm as the reaction occurs. In reaction B, the test tube becomes cold. Which reaction is endothermic and which is exothermic? Explain.
4. Classify "burning paper" as endothermic or exothermic processes.

Answers

1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
2. Energy changes because bonds rearrange to make new bonds with different energies.
3. Reaction A is exothermic because heat is leaving the system making the test tube feel hot. Reaction B is endothermic because heat is being absorbed by the system making the test tube feel cold.
4. "Burning paper" is exothermic because burning (also known as combustion) releases heat

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

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6.23: Why Do Chemical Reactions Occur? Free Energy

Learning Outcomes

- Describe the meaning of a spontaneous reaction in terms of enthalpy and entropy changes.
- Define free energy.
- Determine the spontaneity of a reaction based on the value of its change in free energy at high and low temperatures.

Spontaneous Reactions

A **spontaneous reaction** *is a reaction that favors the formation of products at the conditions under which the reaction is occurring*. A roaring bonfire (see Figure **6.23.1** below) is an example of a spontaneous reaction. A fire is *exothermic*, which means a decrease in the energy of the system as energy is released to the surroundings as heat. The products of a fire are composed mostly of gases such as carbon dioxide and water vapor, so the entropy of the system increases during most combustion reactions. This combination of a decrease in energy and an increase in entropy means that combustion reactions occur spontaneously.



Figure **6.23.1**: Combustion reactions, such as this fire, are spontaneous reactions. Once the reaction begins, it continues on its own until one of the reactants (fuel or oxygen) is gone.

A **nonspontaneous reaction** *is a reaction that does not favor the formation of products at the given set of conditions*. In order for a reaction to be nonspontaneous, one or both of the driving forces must favor the reactants over the products. In other words, the reaction is endothermic, is accompanied by a decrease in entropy, or both. Out atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide.

$$\mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{NO}\,(g) \tag{6.23.1}$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures, it is a highly endothermic reaction. However, nitrogen monoxide is capable of being produced at very high temperatures, and this reaction has been observed to occur as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. You do not have to worry about a piece of paper on your desk suddenly bursting into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

Entropy as a Driving Force

An example of a very simple spontaneous process is that of a melting ice cube. Energy is transferred from the room to the ice cube, causing it to change from the solid to the liquid state.

$$\mathrm{H_2O}\,(s) + 6.01\ \mathrm{kJ} \rightarrow \mathrm{H_2O}\,(l) \tag{6.23.2}$$

The solid state of water, ice, is highly *ordered* because its molecules are fixed in place. The melting process frees the water molecules from their hydrogen-bonded network and allows them a greater degree of movement. Water is more *disordered* than ice.

The change from the solid to the liquid state of any substance corresponds to an increase in the disorder of the system.

The tendency in nature for systems to proceed toward a state of greater disorder or randomness is called **entropy**, which is symbolized by *S*, and expressed in units of Joules per mole-kelvin, $\mathrm{J/(mol \cdot K)}$. Larger values of *S* indicate that the particles in a substance have more disorder or randomness. In the example above, the particles in the ice cube (solid water) have lower freedom of motion, they are less random. As the ice melts to liquid water, the particles become more disordered and entropy increases. If the liquid water was heated further, the particles would even gain more freedom of motion, become more disordered, and eventually change to a gas, which has even higher entropy.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system, measured by the **entropy change (ΔS)** between reactants and products. How can you tell if a certain reaction shows an increase or a decrease in entropy? The states of the reactants and produces provide certain clues. The general cases below illustrate entropy at the molecular level.

1. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.
2. Entropy increases when a substance is broken up into multiple parts. The process of dissolving increases entropy because the solute particles become separated from one another when a solution is formed.
3. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster moving particles have more disorder than particles that are moving more slowly at a lower temperature.
4. Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules. An exception to this rule is when nongaseous products are formed from gaseous reactants.

The examples below will serve to illustrate how the entropy change in a reaction can be predicted.

$$\mathrm{Cl_2}\,(g) \rightarrow \mathrm{Cl_2}\,(l) \tag{6.23.3}$$

The entropy is decreasing because a gas is becoming a liquid.

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \tag{6.23.4}$$

The entropy is increasing because a gas is being produced, and the number of molecules is increasing.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g) \tag{6.23.5}$$

The entropy is decreasing because four total reactant molecules are forming two total product molecules. All are gases.

$$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s) \tag{6.23.6}$$

The entropy is decreasing because a solid is formed from aqueous reactants.

$$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightarrow 2\mathrm{HCl}\,(g) \tag{6.23.7}$$

The entropy change is unknown (but likely not zero) because there are equal numbers of molecules on both sides of the equation, and all are gases.

Gibbs Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** *is energy that is available to do work*. Spontaneous reactions release free energy as they proceed. The determining factors for spontaneity of a reaction depend on both the *enthalpy* and *entropy* changes that occur for the system. The **free energy change (ΔG)** of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6.23.8}$$

The symbol for free energy is G, in honor of American scientist Josiah Gibbs (1839 - 1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change

in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states, as indicated by the ° superscripts.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta H$ indicates that the reaction is exothermic and a $+\Delta H$ means the reaction is endothermic. For entropy, $+\Delta S$ means the entropy is increasing and the system is becoming more disordered. A $-\Delta S$ means that entropy is decreasing and the system is becoming less disordered (more ordered).

> A process that releases free energy, ($-\Delta G$), is said to be ***exergonic***. Processes that require free energy ($+\Delta G$), are ***endergonic***. These terms are used when considering chemical reactions that occur in living systems.

Table **6.23.1**: Enthalpy, Entropy, and Free Energy Changes.

ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

Keep in mind that the temperature in the Gibbs free energy equation is the Kelvin temperature, so it can only have a positive value. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

When one driving force favors the reaction, but the other does not, it is the temperature that determines the sign of ΔG. Consider first an endothermic reaction (positive ΔH) that also displays an increase in entropy (positive ΔS). It is the entropy term that favors the reaction. Therefore, as the temperature increases, the $T\Delta S$ term in the Gibbs free energy equation will begin to predominate and ΔG will become negative. A common example of a process which falls into this category is the melting of ice (see figure below). At a relatively low temperature (below $273\ \text{K}$), the melting is not spontaneous because the positive ΔH term "outweighs" the $T\Delta S$ term. When the temperature rises above $273\ \text{K}$, the process becomes spontaneous because the larger T value has tipped the sign of ΔG over to being negative.



Figure **6.23.2**: Ice melts spontaneously only when the temperature is above 0°C. The increase in entropy is then able to drive the unfavorable endothermic process.

When the reaction is exothermic (negative ΔH) but undergoes a decrease in entropy (negative ΔS), it is the enthalpy term which favors the reaction. In this case, a spontaneous reaction is dependent upon the $T\Delta S$ term being small relative to the ΔH term, so that ΔG is negative. The freezing of water is an example of this type of process. It is spontaneous only at a relatively low temperature. Above $273.\,\mathrm{K}$, the larger $T\Delta S$ value causes the sign of ΔG to be positive, and freezing does not occur.

Contributors and Attributions

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6.24: How Do Chemical Reactions Occur? Reaction Rates

Learning Outcomes

- Define reaction rate.
- Explain the concept of activation energy.
- Label a diagram with reactants, products, enthalpy of forward and reverse reactions, activation energy of forward and reverse reactions, and activated complex.

Chemical kinetics is the study of the rates of chemical reactions. In this lesson, you will learn how to express the rate of a chemical reaction and about various factors that influence reaction rates.

Expressing Reaction Rate

Chemical reactions vary widely in the speeds with which they occur. Some reactions occur very quickly. It a lighted match is brought into contact with lighter fluid or another flammable liquid, it erupts into flame instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes 11.0 seconds (s) to run a 100 meter (\left(m \right)\) dash, his rate or speed is given by the distance traveled divided by the time (see figure below).

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s} \tag{6.24.1}$$

The sprinter's average running rate for the race is $9.09\ \text{m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must the be greater than $9.09\ \text{m/s}$ so that taken over the entire race, the average ends up at $9.09\ \text{m/s}$.

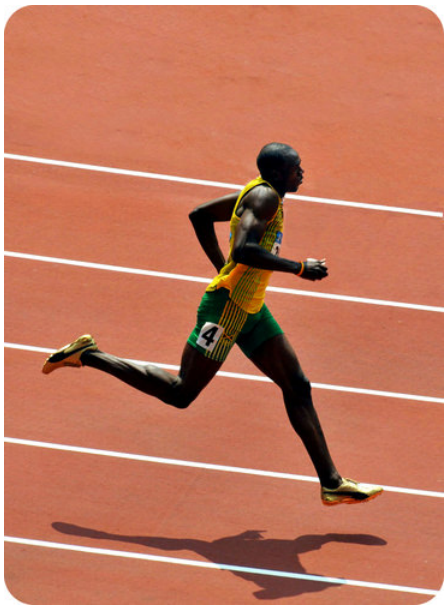


Figure **6.24.1**: Usain Bolt set the world record for the 100 meter dash in 2009 with a time of 9.58 seconds. His average running rate over the course of this race was $10.4\ \text{m/s}$, or $23.4\ \text{mph}$.

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** *is the change in concentration of a reactant or product with time*. Suppose that a simple reaction were to take place in which a 1.00 molar (M) aqueous solution of substance A was converted to substance B.

$$\text{A}\,(aq) \rightarrow \text{B}\,(aq) \tag{6.24.2}$$

Suppose that after 20.0 seconds, the concentration of **A** had dropped from **1.00 M** to **0.72 M** as it was being converted to substance **B**. We can express the rate of this reaction as the change in concentration of **A** divided by the time.

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{[\text{A}]_{\text{final}} - [\text{A}]_{\text{initial}}}{\Delta t} \tag{6.24.3}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of **A** is its final concentration minus its initial concentration. Because the concentration of **A** is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive, and the units are molarity per second or **M/s**.

$$\text{rate} = -\frac{0.72\ \text{M} - 1.00\ \text{M}}{20.0\ \text{s}} = -\frac{-0.28\ \text{M}}{20.0\ \text{s}} = 0.041\ \text{M/s} \tag{6.24.4}$$

Over the first 20.0 seconds of this reaction, the molarity of **A** decreases by an average rate of **0.041 M** every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second **(M/s)**.

Collision Theory

The behavior of the reactant atoms, molecules, or ions is responsible for the rates of a given chemical reaction. **Collision theory** *is a set of principles based around the idea that reactant particles form products when they collide with one another, but only when those collisions have enough kinetic energy and the correct orientation to cause a reaction.* Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other produce. The first collision is called an ineffective collision, while the second collision is called an effective collision.

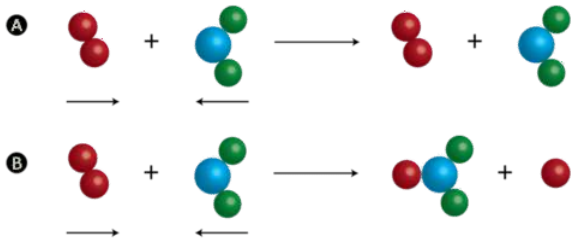


Figure **6.24.2**: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break and a chemical reaction more likely to occur when those particles collide with other particles. Additionally, more energetic particles have more forceful collisions, which also increases the likelihood that a rearrangement of atoms will take place. The **activation energy** *for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction.* Some reactions occur readily at room temperature because most of the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy to react unless more is provided by an external source of heat.

Potential Energy Diagrams

Then energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, sometimes called a reaction progress curve. A **potential energy diagram** *shows the change in the potential energy of a system as reactants are converted into products.* The figure below shows basic potential energy diagrams for an endothermic (left) and an exothermic (right) reaction. Recall that the enthalpy change **(ΔH)** is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

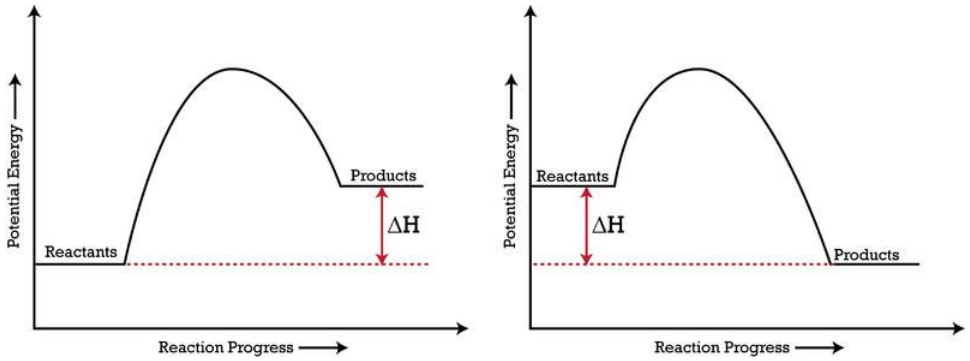


Figure **6.24.3**: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and ΔH is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and ΔH is negative.

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome this barrier (see figure below).

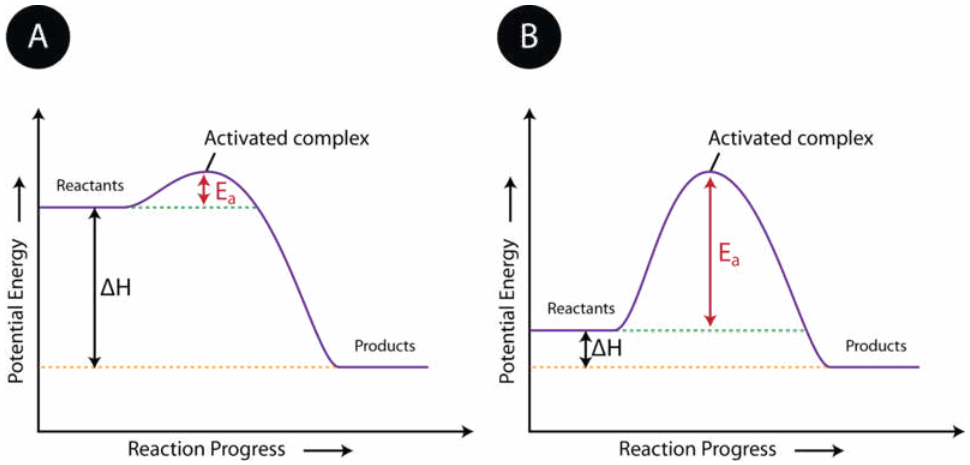


Figure **6.24.4**: The activation energy (E_a) of a reaction is the barrier that must be overcome in order for the reactants to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

As discussed earlier, reactant particles sometimes collide with one another and yet remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** *is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier*. Because of its high energy, the activated complex exists only for an extremely short period of time (about 10^{-13} s). The activated complex is equally likely to either reform the original reactants or go on to form the products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of most activated complexes.

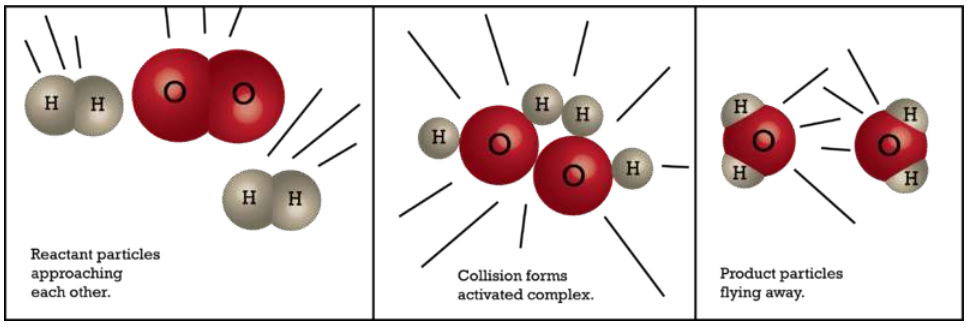


Figure **6.24.5**: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

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6.25: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

Learning Outcomes

- Describe how temperatures, concentration of reactant, and a catalyst affect the reaction rate.

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reaction conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

Concentration

Increasing the concentration of one or more of the reacting substances generally increases the reaction rate. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the frequency of collisions between the reactants, the rate increases as the concentration increases.

Temperature

Raising the temperature of a chemical reaction results in a higher reaction rate. When the reactant particles are heated, they move faster and faster, resulting in a greater frequency of collisions. An even more important effect of the temperature increase is that the collisions occur with a greater force, which means the reactants are more likely to surmount the activation energy barrier and go on to form products. Increasing the temperature of a reaction increases not only the frequency of collisions, but also the percentage of those collisions that are effective, resulting in an increased reaction rate.

Paper is certainly a highly combustible material, but paper does not burn at room temperature because the activation energy for the reaction is too high. The vast majority of collisions between oxygen molecules and the paper are ineffective. However, when the paper is heated by the flame from a match, it reaches a point where the molecules now have enough energy to react. The reaction is very exothermic, so the heat released by the initial reaction will provide enough energy to allow the reaction to continue, even if the match is removed. The paper continues to burn rapidly until it is gone.

Catalysts

The rates of some chemical reactions can be increased dramatically by introducing certain other substances into the reaction mixture. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and it can be found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** *is a substance that increases the rate of a chemical reaction without being used up in the reaction*. It accomplishes this task by providing an alternate reaction pathway that has a lower activation energy barrier. After the reaction occurs, a catalyst returns to its original state, so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$2H_2O_2\,(aq) \overset{MnO_2}{\rightarrow} 2H_2O\,(l) + O_2\,(g) \tag{6.25.1}$$

A catalyst works by changing the mechanism of the reaction, which can be though of as the specific set of smaller steps by which the reactants become products. The important point is that the use of a catalyst lowers the overall activation energy of the reaction (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

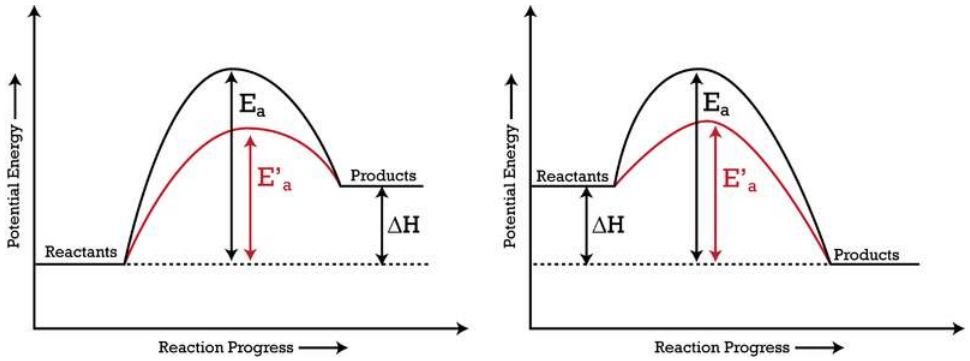


Figure **6.25.7**: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E'_a. The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

Catalysts are extremely important parts of many chemical reactions. Enzymes in your body act as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

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CHAPTER OVERVIEW

7: Gases

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7.4: Charles’s Law- The Relation between Volume and Temperature
7.5: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
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7.8: The Ideal Gas Law
7.9: Partial Pressure and Dalton's Law

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7.1: Gases and the Kinetic-Molecular Theory

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. The kinetic theory of gases is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic—that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 7.1.1 shows a representation of how we mentally picture the gas phase.

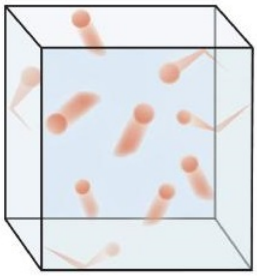


Figure 7.1.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements, and the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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7.2: Pressure

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 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 equivalencies:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

We can use these equivalencies as with any equivalencies—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

Example 7.2.1: Pressure Conversion

How many atmospheres are there in 595 torr?

Solution

Using the pressure equivalencies, we construct a conversion factor between torr and atmospheres:

$$\frac{1\,atm}{760\,torr}$$

$$595\ \cancel{torr} \times \frac{1\,atm}{760\ \cancel{torr}} = 0.783\,atm$$

Because the numbers in the conversion factor are exact, the number of significant figures in the final answer is determined by the initial value of pressure.

Exercise 7.2.1

How many atmospheres are there in 1,022 torr?

Answer

1.345 atm

Example 7.2.2: Mars

The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

Solution

Use the pressure equivalencies to construct the proper conversion factor between millimeters of mercury and atmospheres.

$$6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$$

At the end, we expressed the answer in scientific notation.

Exercise 7.2.2

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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7.3: Boyle's Law - The Relation between Volume and Pressure

Learning Objectives

- Define the relationship between gas volume and pressure, Boyle's Law.
- Use Boyle's Law to calculate changes in pressure or volume of a gas.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (P) and volume (V), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [n]), if the temperature (T) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. We say that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant (k) for a given amount of gas at a constant temperature:

$$P \times V = k \ (at\ constant\ n\ and\ T)$$

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

$$P_1V_1 = k = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \ (at\ constant\ n\ and\ T)$$

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

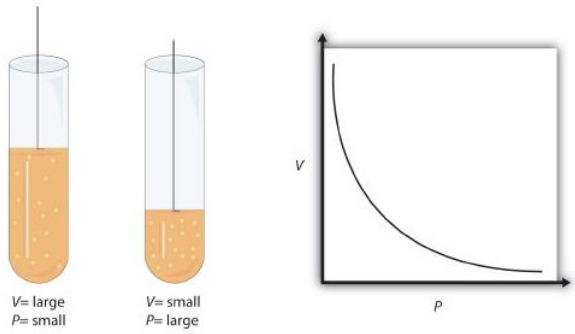


Figure **7.3.1**: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle's law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

Example 7.3.1

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

First, determine what quantities we are given. We are given an initial pressure and an initial volume, so let these values be P_1 and V_1:

$$P_1 = 2.44 \text{ atm and } V_1 = 4.01 \text{ L}$$

We are given another quantity, final pressure of 1.93 atm, but not a final volume. This final volume is the variable we will solve for.

$$P_2 = 1.93 \text{ atm and } V_2 = ? \text{ L}$$

Substituting these values into Boyle's law, we get

$$(2.44 \text{ atm})(4.01 \text{ L}) = (1.93 \text{ atm})V_2$$

To solve for the unknown variable, we isolate it by dividing both sides of the equation by 1.93 atm—both the number *and* the unit:

$$\frac{(2.44\,atm)(4.01\,L)}{1.93\,atm} = \frac{(1.93\,atm)\,V_2}{1.93\,atm}$$

Note that, on the left side of the equation, the unit *atm* is in the numerator and the denominator of the fraction. They cancel algebraically, just as a number would. On the right side, the unit *atm* and the number 1.93 are in the numerator and the denominator, so the entire quantity cancels:

$$\frac{(2.44\,\cancel{atm})(4.01\,L)}{1.93\,\cancel{atm}} = \frac{(1.93\,\cancel{atm})\,V_2}{1.93\,\cancel{atm}}$$

What we have left is

$$\frac{(2.44)(4.01\,L)}{1.93} = V_2$$

Now we simply multiply and divide the numbers together and combine the answer with the L unit, which is a unit of volume. Doing so, we get $V_2 = 5.07\,L$

Does this answer make sense? We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

Exercise 7.3.1

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

Answer

124 mL

As mentioned, you can use any units for pressure or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

Example 7.3.2

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

We can still use Boyle's law to answer this, but now the two volume quantities have different units. It does not matter which unit we change, as long as we perform the conversion correctly. Let us change the 0.663 L to milliliters:

$$0.663\,L \times \frac{1000\,ml}{1\,L} = 663\,ml$$

Now that both volume quantities have the same units, we can substitute into Boyle's law:

$$(722\,torr)(88.8\,ml) = P_2(663\,ml)$$

$$\frac{(722\,torr)(88.8)\,ml}{(663\,ml)} = P_2$$

The mL units cancel, and we multiply and divide the numbers to get P_2 = 96.7 torr

The volume is increasing, and the pressure is decreasing, which is as expected for Boyle's law.

? Exercise 7.3.2

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

Answer

119 mL

To Your Health: Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure **7.3.2**).

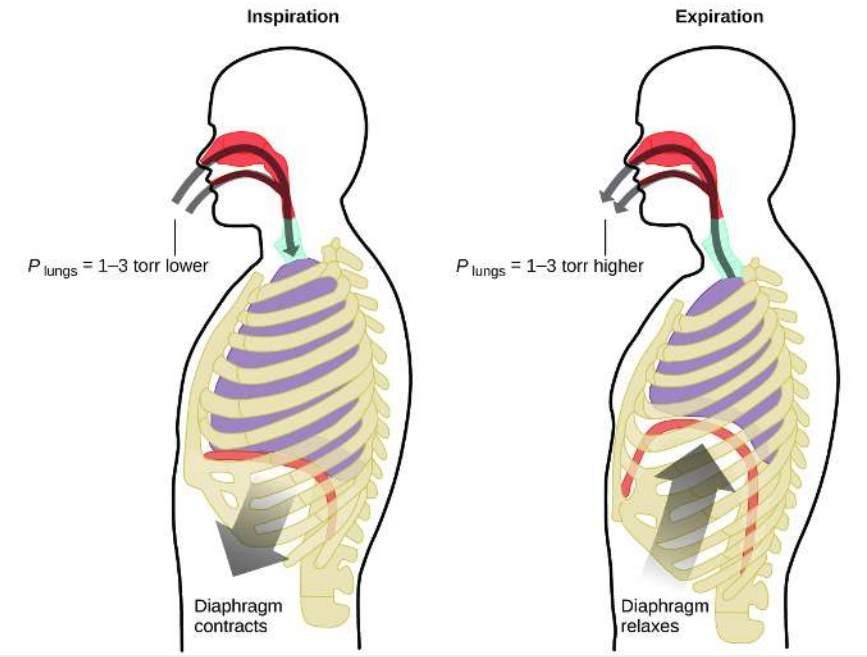


Figure **7.3.2**: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

This figure contains two diagrams of a cross section of the human head and torso. The first diagram on the left is labeled “Inspiration.” It shows curved arrows in gray proceeding through the nasal passages and mouth to the lungs. An arrow points downward from the diaphragm, which is relatively flat, just beneath the lungs. This arrow is labeled “Diaphragm contracts.” At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr lower” is provided. The second, similar diagram, which is labeled “Expiration,” reverses the direction of both arrows. Arrows extend from the lungs out through the nasal passages and mouth. Similarly, an arrow points up to the diaphragm, showing a curved diaphragm and lungs reduced in size from the previous image. This arrow is labeled “Diaphragm relaxes.” At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr higher” is provided.

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's law relates a gas's pressure and volume at constant temperature and amount.

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7.4: Charles's Law- The Relation between Volume and Temperature

Learning Objectives

- Define the relationship between gas temperature and volume, Charles's Law.
- Use Charles's Law to calculate changes in temperature or volume of a gas.

In addition to pressure and volume, another measurable characteristics of a gas is temperature (*T*). Perhaps one can vary the temperature of a gas sample and note what effect it has on the other properties of the gas. Early scientists did just this, discovering that if the amount of a gas and its pressure are kept constant, then changing the temperature changes the volume (*V*). As temperature increases, volume increases; as temperature decreases, volume decreases. We say that these two characteristics are *directly related*.

Kelvin Temperature Scale

A mathematical relationship between *V* and *T* should be possible except for one thought: what temperature scale should we use? We know from previous chapters that scientists uses several possible temperature scales. Experiments show that the volume of a gas is related to its absolute temperature in **Kelvin**, *not its temperature in degrees Celsius*. If the temperature of a gas is expressed in Kelvins, then experiments show that the *ratio* of volume to temperature is a constant (*k*):

$$\frac{V}{T} = k$$

Charles's Law

We can modify this equation as we modified Boyle's law: the initial conditions V_1 and T_1 have a certain value, and the value must be the same when the conditions of the gas are changed to some new conditions V_2 and T_2, as long as pressure and the amount of the gas remain constant. Thus, we have another gas law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \ (at\ constant\ P\ and\ n)$$

This gas law is commonly referred to as **Charles's law**, after the French scientist Jacques Charles, who performed experiments on gases in the 1780s. The tactics for using this mathematical formula are similar to those for Boyle's law. To determine an unknown quantity, use algebra to isolate the unknown variable by itself and in the numerator; the units of similar variables must be the same. But we add one more tactic: all temperatures must be expressed in the absolute temperature scale (Kelvin). As a reminder, we review the conversion between the absolute temperature scale and the Celsius temperature scale:

$$K = °C + 273$$

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius.

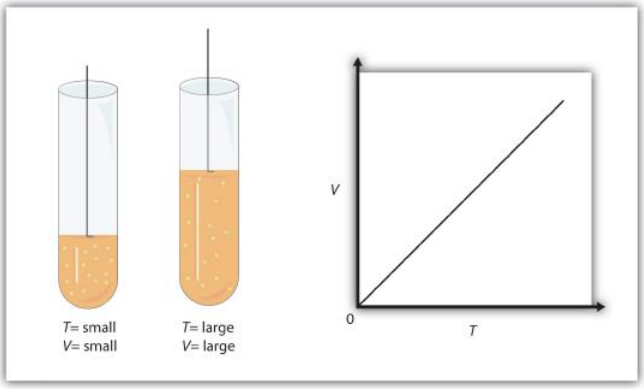


Figure 7.4.1: Charles's Law. A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.

Example 7.4.1

A sample of gas has an initial volume of 34.8 mL and an initial temperature of 315 K. What is the new volume if the temperature is increased to 559 K? Assume constant pressure and amount for the gas.

Solution

First, we assign the given values to their variables. The initial volume is V_1, so V_1 = 34.8 mL, and the initial temperature is T_1, so T_1 = 315 K. The temperature is increased to 559 K, so the final temperature T_2 = 559 K. We note that the temperatures are already given in kelvins, so we do not need to convert the temperatures. Substituting into the expression for Charles's law yields

$$\frac{34.8\,ml}{315\,K} = \frac{V_2}{559\,K}$$

We solve for V_2 by algebraically isolating the V_2 variable on one side of the equation. We do this by multiplying both sides of the equation by 559 K (number and unit). When we do this, the temperature unit cancels on the left side, while the entire 559 K cancels on the right side:

$$\frac{(559\,\cancel{K})(34.8\,ml)}{315\,\cancel{K}} = \frac{V_2(\cancel{559\,K})}{\cancel{559\,K}}$$

The expression simplifies to

$$\frac{(559)(34.8\,ml)}{315} = V_2$$

By multiplying and dividing the numbers, we see that the only remaining unit is mL, so our final answer is

V_2 = 61.8 mL

Does this answer make sense? We know that as temperature increases, volume increases. Here, the temperature is increasing from 315 K to 559 K, so the volume should also increase, which it does.

Exercise 7.4.1

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

Answer

1.82 L

It is more mathematically complicated if a final temperature must be calculated because the T variable is in the denominator of Charles's law. There are several mathematical ways to work this, but perhaps the simplest way is to take the reciprocal of Charles's law. That is, rather than write it as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

write the equation as

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

It is still an equality and a correct form of Charles's law, but now the temperature variable is in the numerator, and the algebra required to predict a final temperature is simpler.

Example 7.4.2

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must the temperature of the gas be for its volume to be 25.0 L?

Solution

Here, we are looking for a final temperature, so we will use the reciprocal form of Charles's law. However, the initial temperature is given in degrees Celsius, not kelvins. We must convert the initial temperature to kelvins:

−67°C + 273 = 206 K

In using the gas law, we must use T_1 = 206 K as the temperature. Substituting into the reciprocal form of Charles's law, we get

$$\frac{206\,K}{34.8\,L} = \frac{T_2}{25.0\,L}$$

Bringing the 25.0 L quantity over to the other side of the equation, we get

$$\frac{(25.0\,\cancel{L})(206\,K)}{34.8\,\cancel{L}} = T_2$$

The L units cancel, so our final answer is T_2 = 148 K

This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

? Exercise 7.4.2

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 a gas's volume and temperature at constant pressure and amount.
- In gas laws, temperatures must always be expressed in kelvins.

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7.5: Gay-Lussac's Law- The Relationship Between Pressure and Temperature

Learning Objectives

- Define the relationship between gas pressure and temperature, Gay-Lussac's Law.

A third gas law may be derived as a corollary to Boyle's and Charles's laws. Suppose we double the thermodynamic temperature of a sample of gas. According to Charles's law, the volume should double. Now, how much pressure would be required at the higher temperature to return the gas to its original volume? According to Boyle's law, we would have to double the pressure to halve the volume. Thus, if the volume of gas is to remain the same, doubling the temperature will require doubling the pressure. This law was first stated by the Frenchman Joseph Gay-Lussac (1778 to 1850). According to **Gay-Lussac's law**, *for a given amount of gas held at constant volume, the pressure is proportional to the absolute temperature.* Mathematically,

$$P \propto T \text{ or } P = k \times T \text{ or } \frac{P}{T} = k$$

where $\propto$ means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

In terms of two sets of data: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Gay-Lussac's law tells us that it may be dangerous to heat a gas in a closed container. The increased pressure might cause the container to explode, as you can see in the video below. The video shows very, very cold nitrogen gas in a bottle being warmed by the air. Since the bottle's volume is relatively constant, as the temperature of the nitrogen gas (formed when the liquid nitrogen boils) increases, so does the pressure inside the bottle until, finally, BOOM!



Example 7.5.1: Temperature

A container is designed to hold a pressure of 2.5 atm. The volume of the container is 20.0 cm^3, and it is filled with air at room temperature (20°C) and normal atmospheric pressure. Would it be safe to throw the container into a fire where temperatures of 600°C would be reached?

Solution

Using the common-sense method, we realize that the pressure will increase at the higher temperature, and so:

$$P_2 = 1.0 \text{ atm} \times \frac{(273.15 + 600) \text{ K}}{(273.15 + 20) \text{ K}} = 3.0 \text{ atm}$$

This would exceed the safe strength of the container. Note that the volume of the container was not needed to solve the problem.

This concept works in reverse, as well. For instance, if we subject a gas to lower temperatures than their initial state, the external atmosphere can actually force the container to shrink. The following video demonstrates how a sample of hot gas, when cooled will collapse a container. A syringe barrel is filled with hot steam (vaporized water) and a plunger placed to cap off the end. The syringe is then placed in a beaker of ice water to cool the internal gas. When the temperature of the water vapor decreases, the pressure exerted by the vapor decreases as well. This leads to a difference in pressure between the vapor inside the barrel and the atmosphere. Atmospheric pressure then pushes the plunger into the barrel.

Summary

- Gay-Lussac's law relates a gas's temperature and pressure at constant volume and amount.
- In gas laws, temperatures must always be expressed in kelvins.

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7.6: The Combined Gas Law

Learning Objectives

- Use the combined gas law to determine the relationships between pressure, volume, and temperature of a gas.

One thing we notice about all gas laws, collectively, is that 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:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ at constant } n$$

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 kelvins.

Notice that each of the previous gas laws introduced, can be derived from the combined gas law:

At constant T, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* **Boyle's Law:** $P_1V_1 = P_2V_2$

At constant P, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* **Charles's Law:** $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

At constant V, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* **Gay-Lussac's Law:** $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

In other words, if you know the equation for the combined gas law, you can calculate relationships between pressure, volume, or temperature of a fixed amount of gas.

Example 7.6.2

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

We can use the combined gas law directly; all the units are consistent with each other, and the temperatures are given in Kelvin. Substituting,

$$\frac{(1.82\,atm)(8.33\,L)}{286\,K} = \frac{P_2(5.72\,L)}{355\,K}$$

We rearrange this to isolate the P_2 variable all by itself. When we do so, certain units cancel:

$$\frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})} = P_2$$

Multiplying and dividing all the numbers, we get

$$P_2 = 3.29\,atm$$

Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

Exercise 7.6.2

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

Summary

- There are gas laws that relate any two physical properties of a gas.
- The combined gas law relates pressure, volume, and temperature of a gas.

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7.7: Avogadro’s Law - The Relation between Volume and Molar Amount

Learning Objectives

- Describe the relationship between the amount and volume of a gas, Avogadro's Law.
- Define the conditions of standard temperature and pressure.

The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac’s work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure **7.7.1**). This is the historic “Avogadro’s hypothesis.”

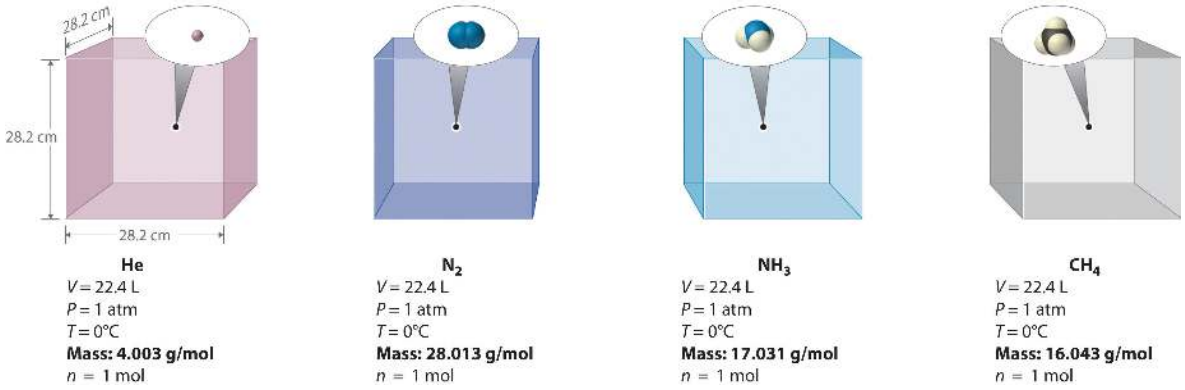


Figure **7.7.1**: Avogadro’s Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

Because the number of particles is related to the number of moles (1 mol = 6.022×10^{23} particles), **Avogadro's law** essentially states that equal volumes of different gases, at the same temperature and pressure, contain the same *amount* (moles, particles) of gas. *At constant temperature and pressure, the volume (V) of a sample of gas is directly proportional to the number of moles (n) of gas in the sample.* Stated mathematically,

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V}{n} = k$$

where $\propto$ means “is proportional to,” and k is a proportionality constant that is the same for all gases.

In terms of two sets of data: $\frac{V_1}{n_1} = \frac{V_2}{n_2}$.

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures. Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T.

> *Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).*

Standard Temperature and Pressure

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure**

(STP) is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V = (1\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(273\,K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 7.7.1). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

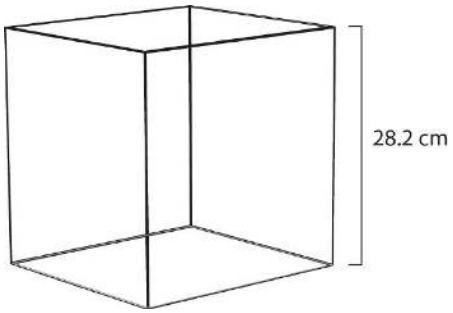


Figure 7.7.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

✔ Example 7.7.4

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7\,\cancel{L} \times \frac{1\,mol}{22.4\,\cancel{L}} = 1.73\,mol$$

? Exercise 7.7.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

✔ Example 7.7.5

What volume of H_2 is produced at STP when 55.8 g of Zn metal react with excess HCl?

$$Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\ \cancel{g\ Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.41\ \cancel{g\ Zn}} \times \frac{1\ mol\ H_2}{1\ \cancel{mol\ Zn}} = 0.853\ H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\ \cancel{mol\ H_2} \times \frac{22.4\ L}{1\ \cancel{mol\ H_2}} = 19.1\ L\ H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

? Exercise 7.7.5

What volume of $\mathbf{HCl}$ is generated if 3.44 g of $\mathbf{Cl_2}$ are reacted at STP?

$$\mathbf{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

Answer

2.17 L

Summary

- Avogadro's law states that the volume of gas is directly proportional to the number of moles of gas.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.

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7.8: The Ideal Gas Law

Learning Objectives

- Describe the ideal gas law.
- Use the ideal gas law to calculate pressure, volume, temperature, or moles of an ideal gas.

So far, the gas laws we have considered have all required that the gas change its conditions; then we can predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant \(*R*\) is called the **ideal gas law constant**. Its value depends on the units used to express pressure and volume.

Table **7.8.1**: Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	$\frac{L \cdot atm}{mol \cdot K}$
62.36	$\frac{L \cdot torr}{mol \cdot K} = \frac{L \cdot mmHg}{mol \cdot K}$
8.314	$\frac{J}{mol \cdot K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvin. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 7.8.1

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

The first step is to convert temperature to kelvins:

$$34 + 273 = 307\,\text{K}$$

Now we can substitute the conditions into the ideal gas law:

$$(1.21 atm)(V) = (4.22\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(307\,K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L$$

Then solving for volume, we get V = 87.9 L

? Exercise 7.8.1

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

✓ Example 7.8.2

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\,\cancel{g\,Hg} \times \frac{1\,mol\,Hg}{200.59\,\cancel{g\,Hg}} = 0.0000165\,mol = 1.65 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\,mm\,Hg)(435\,L) = (1.65 \times 10^{-5} mol)(62.36 \frac{L.mmHg}{mol.K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)} K$$

Then solving for K, we get T = 1,404 K.

? Exercise 7.8.2

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

The ideal gas law can also be used in stoichiometry problems.

✓ Example 7.8.3

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is calculated:

$$55.8\,\cancel{g\,Zn} \times \frac{1\,\cancel{mol\,Zn}}{65.41\,\cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1\,\cancel{mol\,Zn}} = 0.853\,H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07atm)V = (0.853\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(299\,K)$$

All the units cancel except for L, for volume, which means V = 19.6 L

? Exercise 7.8.3

What pressure of $\mathbf{HCl}$ is generated if 3.44 g of $\mathbf{Cl_2}$ are reacted in 4.55 L at 455 K?

$$\mathbf{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

Answer

0.796 atm

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems with chemical reactions that involve gases.

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7.9: Partial Pressure and Dalton's Law

Learning Objective

- Define Dalton's law of partial pressures.
- Use Dalton's law to calculate partial pressure of a gas in a mixture.

One of the properties of gases is that they mix with each other. When they do so, they become a solution—a homogeneous mixture. Some of the properties of gas mixtures are easy to determine if we know the composition of the gases in the mix.

In gas mixtures, each component in the gas phase can be treated separately because, according to the kinetic theory of gases, there are little to no attractive or repulsive forces between particles. Each component of a gas mixture shares the same temperature and volume, (remember that gases expand to fill the volume of their container; gases in a mixture continue to do that as well). However, each individual gas will have its *own pressure* within a mixture. This is called the **partial pressure** of a gas, P_i. Partial pressures are expressed in torr, millimeters of mercury, or atmospheres like any other gas pressure; however, we use the term *pressure* when talking about pure gases and the term *partial pressure* when we are talking about the individual gas components in a mixture.

Dalton's law of partial pressures states that the total pressure of a gas mixture, P_{tot}, is equal to the sum of the partial pressures of the components, P_i:

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 ... = \sum_i P_i$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i$$

where i counts over all gases in mixture.

Although this law may seem trivial, it reinforces the idea that gases behave independently of each other.

Example 7.9.1

A mixture of H_2 at 2.33 atm and N_2 at 0.77 atm is in a container. What is the total pressure in the container?

Solution

Dalton's law of partial pressures states that the total pressure is equal to the sum of the partial pressures. We simply add the two pressures together:

P_{tot} = 2.33 atm + 0.77 atm = 3.10 atm

Exercise 7.9.1

N_2 and O_2. In 760 torr of air, the partial pressure of N_2 is 608 torr. What is the partial pressure of O_2?

Answer

152 torr

Example 7.9.2

A 2.00 L container with 2.50 atm of H_2 is connected to a 5.00 L container with 1.90 atm of O_2 inside. The containers are opened, and the gases mix. What is the final pressure inside the containers?

Solution

Because gases act independently of each other, we can determine the resulting final pressures using Boyle's law and then add the two resulting pressures together to get the final pressure. The total final volume is 2.00 L + 5.00 L = 7.00 L. First, we use Boyle's law to determine the final pressure of H_2:

$$(2.50 \text{ atm})(2.00 \text{ L}) = P_2(7.00 \text{ L})$$

Solving for P_2, we get $P_2 = 0.714$ atm = partial pressure of H_2.

Now we do that same thing for the O_2:

$$(1.90 \text{ atm})(5.00 \text{ L}) = P_2(7.00 \text{ L}) P_2 = 1.36 \text{ atm} = \text{partial pressure of } O_2$$

The total pressure is the sum of the two resulting partial pressures:

$$P_{tot} = 0.714 \text{ atm} + 1.36 \text{ atm} = 2.07 \text{ atm}$$

? Exercise 7.9.2

If 0.75 atm of He in a 2.00 L container is connected to a 3.00 L container with 0.35 atm of Ne and the containers are opened, what is the resulting total pressure?

Answer

0.51 atm

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + ... + P_n$$

or

$$P_n = \frac{n}{P_{Total}}$$

Table 7.9.1: Partial Pressures for the gases in air on a typical day

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	P_{O_2} = 160	21
Carbon Dioxide, CO_2	P_{CO_2} = 0.25	0.033
Water Vapor, H_2O	P_{H_2O} = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

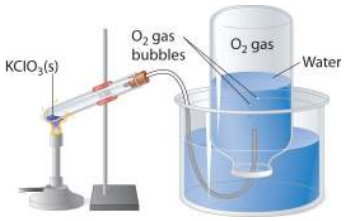


Figure **7.9.1**:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

✔ Example 7.9.3

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

Solution

From Dalton's law,

$$P_{O_2} = P_{total} – P_{H_2O} = 754 – 19.8 = 734\ torr = 0.966\ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latmmol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

? Exercise 7.9.3

CO_2, generated by the decomposition of $CaCO_3$, is collected in a 3.50 L container over water. If the temperature is 50°C and the total pressure inside the container is 833 torr, how many moles of CO_2 were generated?

Answer

0.129 mol

✔ Food and Drink Application: Carbonated Beverages

Carbonated beverages—sodas, beer, sparkling wines—have one thing in common: they have CO_2 gas dissolved in them in such sufficient quantities that it affects the drinking experience. Most people find the drinking experience pleasant—indeed, in the United States alone, over 1.5×10^9 gal of soda are consumed each year, which is almost 50 gal per person! This figure does not include other types of carbonated beverages, so the total consumption is probably significantly higher.

All carbonated beverages are made in one of two ways. First, the flat beverage is subjected to a high pressure of CO_2 gas, which forces the gas into solution. The carbonated beverage is then packaged in a tightly-sealed package (usually a bottle or a can) and sold. When the container is opened, the CO_2 pressure is released, resulting in the well-known *hiss* of an opening container, and CO_2 bubbles come out of solution. This must be done with care: if the CO_2 comes out too violently, a mess can occur!



Figure 7.9.1: Carbonated beverage. If you are not careful opening a container of a carbonated beverage, you can make a mess, as the CO_2 comes out of solution suddenly. (Unsplash License; Tina Vanhove via Unsplash)

The second way a beverage can become carbonated is by the ingestion of sugar by yeast, which then generates CO_2 as a digestion product. This process is called *fermentation*. The overall reaction is

$$C_6H_{12}O_6\,(aq) \longrightarrow 2\,C_2H_5OH\,(aq) + 2\,CO_2\,(aq)$$

When this process occurs in a closed container, the CO_2 produced dissolves in the liquid, only to be released from solution when the container is opened. Most fine sparkling wines and champagnes are turned into carbonated beverages this way. Less-expensive sparkling wines are made like sodas and beer, with exposure to high pressures of CO_2 gas.

Summary

- The pressure of a gas in a gas mixture is termed the *partial pressure*.
- Dalton's law of partial pressure says that the total pressure in a gas mixture is the sum of the individual partial pressures.

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CHAPTER OVERVIEW

8: Solutions

8.1: Introduction to solution

8.2: Solubility

8.3: Electrolytes

8.4: Concentration of solutions

8.5: Osmosis

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8.1: Introduction to solution

Solutions are all around us, e.g., air, seawater, body fluids, metal alloys are solutions. Fig. 5.1.1 illustrates that air is a mixture of nitrogen, oxygen, carbon dioxide, and some other gases; Fig. 5.1.2 illustrates that seawater is a mixture of water, chloride, sodium, sulfate, magnesium, and some other ions, and Fig. 5.1.3. illustrates that about 60% of the human body is composed of solutions called body fluids.

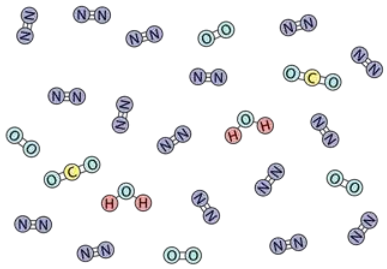


Figure **8.1.1**: Air is a solution of nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and some other gases . Source: RoRo / CC0

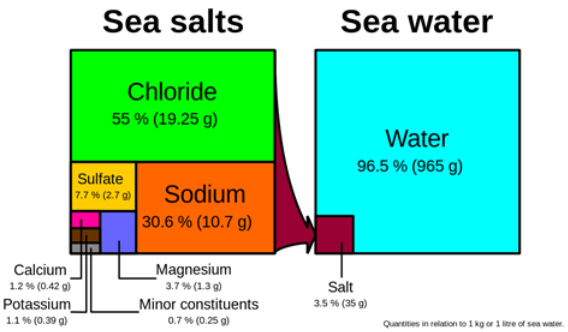


Figure **8.1.2**: Seawater is a solution of water and several ions, expressed in wt/wt%. Source: derivative work: Tcncv (talk)Sea_salt-e_hg.svg: Hannes Grobe, Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany; SVG version by Stefan Majewsky / CC BY-SA (https://creativecommons.org/licenses/by-sa/2.5)

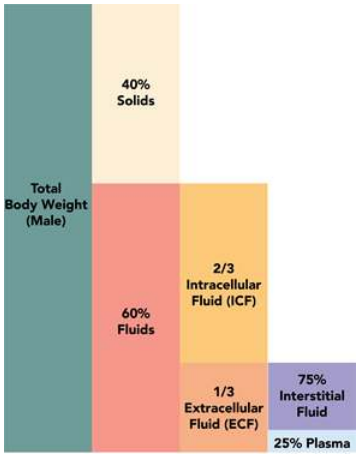


Figure **8.1.3**: This schematic shows the relative volumes of the different fluid compartments in an adult male. Source: Alan Sved and David Walsh / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

What is a solution?

- A solution is a homogeneous mixture of two or more pure substances.
- The substance that is in a large amount in the solution is called the **solvent**.
- The substance that is in smaller amounts in a solution is called the **solute**.

For example, the air is a solution in which nitrogen is the solvent, and water is the solvent in seawater and body fluids. Oxygen, carbon dioxide, and water vapors are solutes in the air; and sodium, chloride, sulfate, magnesium, and some other ions are solutes in seawater.

Types of solution

The solutions are generally classified in two ways: i) based on the physical state of the solution and the solute, and ii) based on the particle size of the solute.

Types of solution based on the physical state of the solution and the solute

The solutions can be classified based on the physical state of the solution, solvent, and solute. For example, the air is gas in a gas solution; carbonated water is a gas in a liquid solution; vinegar is a liquid in a liquid solution; metal alloys are solid in solid solutions. Table 5.1.1 lists the major types of solutions, solvents, and primary solutes in them.

Table 1: Examples of main types of solutions and solvent and major solute in them.

Type	Example	solvent	Primary solute
Gas in gas	Air	Nitrogen	Oxygen
Gas in liquid	Carbonated water	Water	Carbon dioxide
Liquid in liquid	Vinegar	Water	Acetic acid
Solid in liquid	Seawater	Water	Sodium chloride
Solid in solid	Brass	Copper	Zinc

Types of solutions based on the particle size of the solute

Solution

A solution is a homogeneous mixture comprising smaller component/s called solute/s of small molecules or ions comparable in size to the molecules of a larger component called the solvent.

For example, NaCl dissolved in water is a solution. The solute is almost uniformly distributed in the solvent, making a homogeneous mixture. The solute does not separate by filtration or by a semipermeable membrane but can be separated by some other physical process. For example, the distillation process separates a solid in a liquid or a liquid into a liquid solution. The solution is transparent, though it may be colored. A light passing through a solution is not visible, as shown in Fig. 5.1.4.

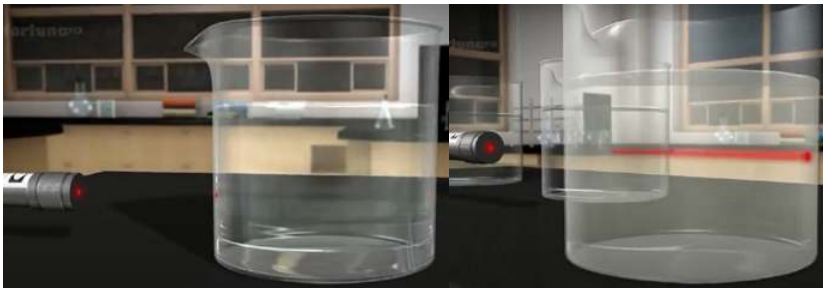


Figure **8.1.4**: Demonstration of Tyndall effect: a red-laser bean passing through a solution is not visible (left), but visible when passing through a colloid (right). Source: https://youtu.be/8Xcpq6e8pBY, Creative Commons Attribution license (reuse allowed)

Suspension

A suspension is a heterogeneous mixture of solvent and solute particles of larger than 10,000 Å.

For example, muddy water is a suspension. If the suspension is allowed to stand, the suspended particles settle down and separate. The suspended particles can be filtered out. Some medicines, e.g., milk of magnesia, are suspensions. It is instructed to shake just before administering medicine to re-suspend the settled suspension.

Colloid

A colloid falls between a solution and a suspension. The colloidal particles are larger molecules like proteins or groups of molecules or ions.

Unlike a suspension, the colloids usually do not settle if allowed to stand. The colloidal particles can not be filtered but can be separated by a semipermeable membrane. When a light beam passes through a colloid, it scatters by the colloid particles, called the Tyndall effect, and becomes visible, as shown in Fig. 5.1.4.

Examples of colloids include:

1. fog and clouds that are liquid water droplets dispersed in air;
2. smoke that is solid carbon particles dispersed in air;
3. whipped cream that is air dispersed in a liquid;
4. styrofoam is a gas dispersed in a solid; and
5. ager medium that is liquid dispersed in a solid medium.
6.

Water –a universal solvent

Water (H_2O) is an essential substance for life. It covers more than 70% of the earth's surface (Fig. 5.1.5), and it comprises more than 60% of the human body (5.1.3). In addition to being the most abundant solvent, water is a universal solvent because it is a polar molecule with a partial negative charge on oxygen and a partial positive charge on hydrogen atoms as shown in Fig. 5.1.6. The polarity of water molecules allows them to interact with other water molecules as well as with other polar compounds through dipole-dipole interactions and with other ions through ion-dipole interactions. These interactions help to dissolve a lot of polar and ionic compounds that are in and around us.



Figure **8.1.5**: the image of the earth showing saltwater in the sea, fresh water on the Antarctic ice sheet, and clouds. Source: by NASA mission AS17. Public domain.

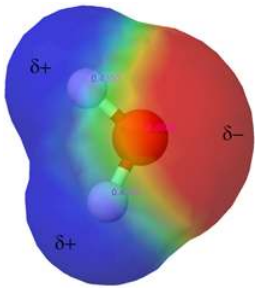


Figure **8.1.6**: A model of water molecule showing oxygen in red and hydrogen in white color balls overplayed with an electrostatic potential map showing the partial positive (+d) region in red and the partial negative (-d) region in blue, drawn using a free web app **https://molview.org**

How does water dissolves polar and ionic compounds?

Water molecules establish electrostatic interaction, called hydrogen bonding, through the partial +ve end of one molecule with a partial –ve end of a neighboring molecule. These interactions impart unique properties to water, like its relatively higher boiling point and melting point compared to other substances of similar molecular weight. Other polar substances have similar interactions, e.g., ethanol has hydrogen bonding similar to water as illustrated in Fig. 5.1.7.

Dissolution of polar substance in water

When water mixes with other polar substances, like ethanol, some of the hydrogen bonding between water molecules replace with similar hydrogen bonding with ethanol molecules. Since the electrostatic potential energy is similar, the natural tendency to go towards more dispersion drives the dispersion of ethanol molecules uniformly in water resulting in the solution.

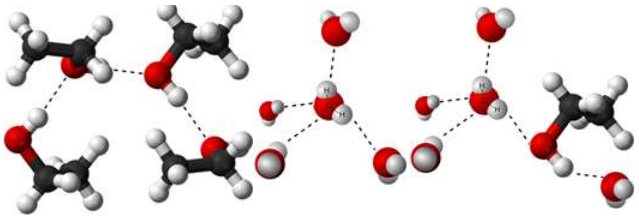


Figure 8.1.7: Models showing hydrogen bonding in ethanol (left), water (middle), and ethanol water solution (right). Source: modified from Benjah-bmm27, and snek01. Public domain

Ionic compounds are held together by electrostatic forces between opposite ions, i.e., ionic bonds. When an ionic compound is added to water, water molecules surround the cation and establish ion-dipole interaction by orienting their partial -ve end to the cation. Similarly, water molecules establish ion-dipole interaction with anions by orienting their partial +ev end towards the anion, as illustrated in Fig. 5.1.8

Dissolution of ionic compounds in water

The ion-dipole interactions, along with nature's tendency to disperse the particles, are usually strong enough to overcome the ionic bonds, dissociate the compounds into ions, and disperse them almost uniformly in the water.

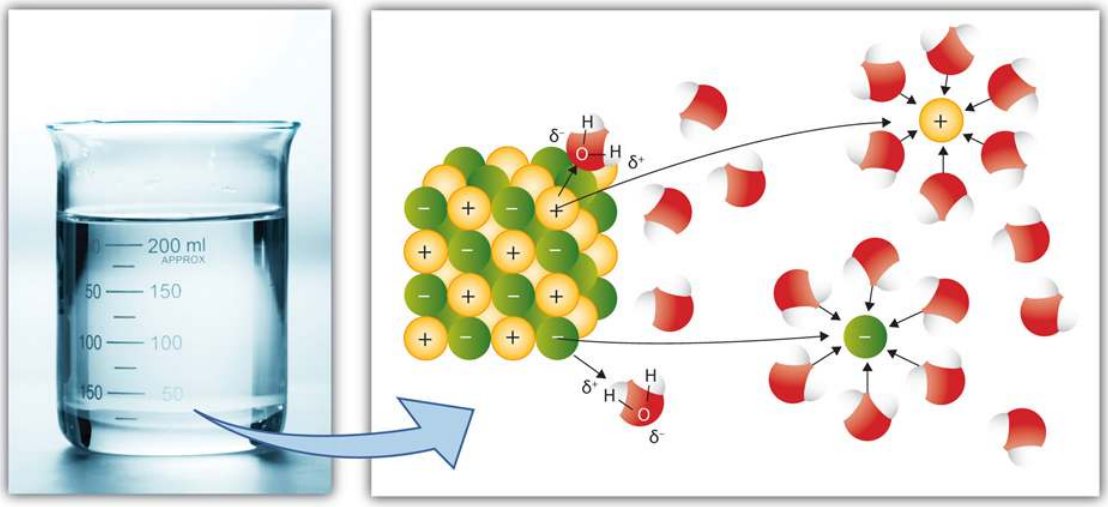


Figure 8.1.8: Dissolution of sodium chloride in water through dissociation into ions and dispersion in water driven by ion-dipole interactions and nature's tendency to disperse particles. Source: Andy Schmitz / CC BY (https://creativecommons.org/licenses/by/3.0)

The separation of the cations from the anions of the ionic compound is called dissociation.

The formation of a layer of water molecules around ions, driven by ion-dipole interactions, is called hydration.

Non-polar substances, like vegetable oil or gasoline, do not dissolve in water. The molecules in non-polar substances have only London dispersion forces. They easily dissolve in non-polar solvents like hexane or carbon tetrachloride that have similar London dispersion forces among their molecules.

The fact that ionic and polar substances dissolve in polar solvents and non-polar substances dissolve in non-polar solvents of similar intermolecular interactions is called "**like dissolves like**."

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8.2: Solubility

Solubility and its related terminologies

The majority of solutes do not dissolve in water or other solvents in all proportions.

What is solubility

The maximum proportion of the solute that can dissolve in a given amount of the solvent, usually expressed in grams of solute in 100 grams of solvent, is called the **solubility** of the solute in the solvent.

1. Substances that make a solution when mixed in any proportion are called **miscible**. For example, ethanol and water are miscible.
2. Some substances make a solution when mixed in some proportion but not in all proportions; these are called **partially miscible**. For example, n-butanol can mix in water up to 7.3 g n-butanol/100 ml water.
3. Substances that almost do not dissolve in each other are called **immiscible**. For example, n-Hexane is immiscible in water.
4. The solution that has not yet reached its solubility limits and can dissolve more solute added is called an **unsaturated solution**.
5. The solution that has reached its solubility limits and can not dissolve if more solute is added to it is called a **saturated solution**.

When a solute is added to a saturated solution, it does dissolve, but, at the same time, the dissociated components recombine to form the crystals of the solute, i.e., recrystallize, at the same rate, so that there is no net dissolution, as illustrated in Fig. 5.2.1.

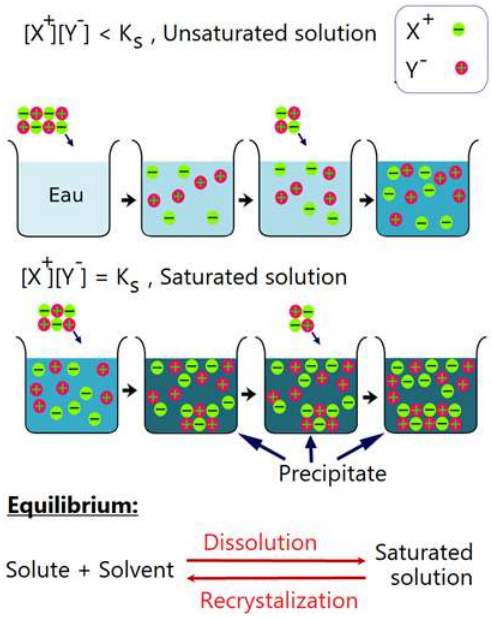


Figure **8.2.1**: Illustration of unsaturated and saturated solution and the dynamic equilibrium between dissolution and recrystallization in the saturated solution. Source: No machine-readable author provided. Romary assumed (based on copyright claims). / CC BY-SA (http://creativecommons.org/licenses/by-sa/3.0/)

Effect of temperature on solubility

The solubility of most of the solids and liquids increases as the temperature increases.

For example, when a saturated solution of sugar in water is heated, it can dissolve more sugar. Fig 5.2.2 show the solubility vs temperature curves for some compounds.

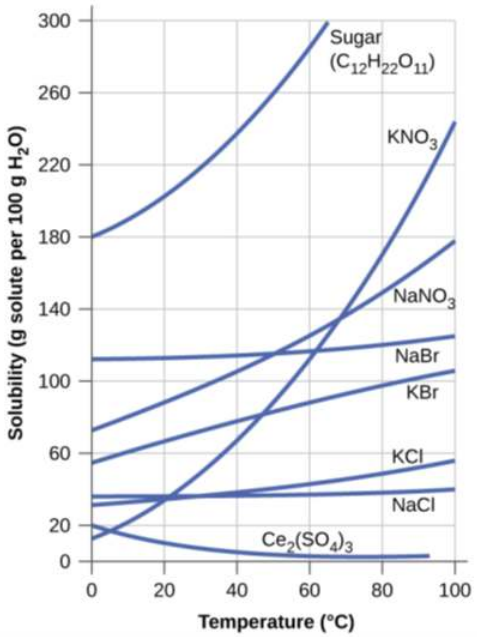


Figure **8.2.2**: Solubility of some ionic and polar molecular compounds in water as a function of temperature. Download for free at https://openstax.org/details/books/chemistry.

When a hot saturated solution is cooled, the concentration of solute in the solution becomes above the solubility limits, making a **supersaturated solution**.

The supersaturated solution is unstable and ultimately crystallizes out the excess solute leaving any impurities in the solution, as illustrated in Fig. 5.2.3. This process is called re-crystallization, which is used to purify the solutes.



Figure **8.2.3**: Salicylic acid recrystallized in water. Source: https://www.youtube.com/watch?v=QwqvzfPneUo

Medical issues related with solubility

The crystallization of excess solute from a supersaturated solution is responsible for some medical problems like gout and kidney stone. Gout is the crystallization of uric acid in the cartilage, tendons, and soft tissues when the concentration of the uric acid in blood plasms exceeds its solubility limit of ~7 mg/100 mL at 37 ^{o}C. It causes redness, swelling, and pain in the affected area, as illustrated in Fig. 5.2.4. Kidney stones are solid materials formed in the urinary tubes, as illustrated in Fig. 5.2.5. Kidney stones are the result of the crystallization of excess calcium phosphate, calcium oxalate, or uric acid in the urine.



Figure 8.2.4: Illustration of gout as a result of the recrystallization of uric acid in the cartilage, tendons, and soft, causes swelling, joint stiffness, and aching around the joint in the foot. Source: www.scientificanimations.com/ / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

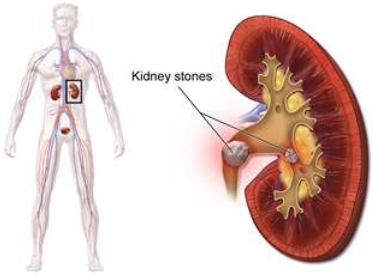


Figure 8.2.5: Kidney Stones illustrated. Source: Blausen.com staff (2014). "Medical gallery of Blausen Medical 2014". WikiJournal of Medicine 1 (2). DOI:10.15347/wjm/2014.010. ISSN 2002-4436/ CC BY (https://creativecommons.org/licenses/by/3.0)

Opposite to the solids and liquids, the solubility of gases generally decreases with an increase in temperature.

That is why the carbonated water releases dissolved gas when heated, causing pressure increase, which, in turn, causes the bursting of the soda can

Effect of pressure on solubility

The pressure has almost no effect on the solubility of solids and liquids but has a strong effect on the solubility of gases.

Henry's law

The solubility of gases in liquids is directly proportional to the pressure of the gas above the liquid.

An increase in pressure causes a decrease in the gas volume that increases the gas concentration. More frequent collision of the gas molecules with the gas-liquid boundary in a concentrated solution causes an increase in the rate of dissolution of the gas in the liquid, as illustrated in Fig 5.2.6. The opposite happens when the gas pressure decreases. For example, carbon dioxide starts bubbling out when a soda can is open because the gas escapes resulting in a decrease in the gas pressure above the liquid and a decrease in the solubility of the gas in water.

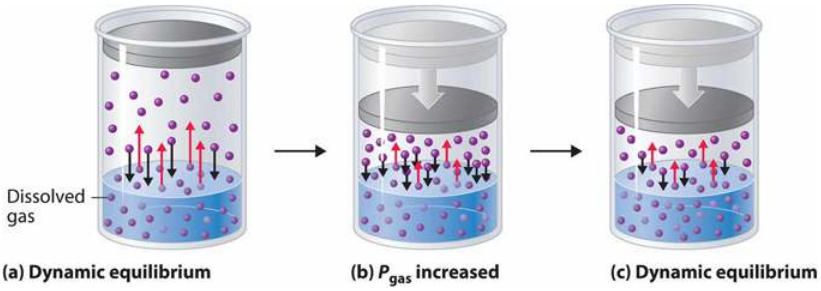


Figure 8.2.6: The Solubility of a gas increases as the partial pressure increases at a constant temperature. Source: Abozenadah, H., Bishop, A., Bittner, S. and Flatt, P.M. (2017) Preparatory Chemistry. CC BY-NC-SA. Available at: https://wou.edu/chemistry/courses/on...ory-chemistry/

Solubility guidelines for dissolution of ionic compounds in water

If the solubility of a compound is less than 0.01 mol/L, it is considered **insoluble**.

The solubility of ionic compounds in water depends on the nature of the compound. For example, lead(II)iodide (PbI_2) and silver chloride (AgCl) are insoluble in water because the solubility of PbI_2 is 0.0016 mol/L of the solution and the solubility of AgCl is about 1.3 x 10^{-5} mol/L of solution. Potassium iodide (KI) and $Pb(NO_3)_2$ are soluble in water. When aqueous solutions of KI and $Pb(NO_3)_2$ are mixed, the concentration of PbI_2 in the mixture goes above its solubility limits, and it precipitates out, as illustrated in Fig. 5.2.7.



Figure **8.2.7**: Precipitation reaction: $\mathbf{Pb(NO_3)_2\,(aq) + 2\,KI\,(aq) \longrightarrow PbI_2(s)\,(v) + 2\,KNO_3\,(aq)}$. source: PRHaney [CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)]

There are no fail-proof guidelines for predicting the solubility of ionic compounds in water. However, the following guideline can predict the solubility of most ionic compounds.

Soluble ions

1. Salts of alkali metals (Li^{1+}, Na^{1+}, K^{1+}, Rb^{1+}, Cs^{1+}) and ammonia (NH_4^{1+}) are soluble. No exceptions.
2. Salts of nitrate (NO_3^{1-}), acetate (CH_3COO^{1-}), and perchlorate (ClO_4^{1-}) are soluble. No exceptions.
3. Salts of chloride (Cl^{1-}), bromide (Br^{1-}), and Iodide (l^{1-}) are soluble, except when the cation is Pb^{2+}, Hg_2^{2-}, or Ag^{1+}. (Remember the acronym “LMS” based on the first letter of the element name, or phrase ‘Let Me See” to recall Lead, Mercury, and Silver.)
4. Sulfates (SO_4^{2-}) are soluble except when the cation Pb^{2+}, Hg_2^{2-}, Ag^{1+}, or a heavy alkaline earth metal ions: calcium (Ca^{2+}), barium (Ba^{2+}), or strontium (Sr^{2+}). ((recall “Let Me See” for Lead, Mercury, and Silver. Remember the acronym “CBS” based on the first letter of the element name, or the phrase “Come By Soon” to recall calcium, barium, and strontium.)

Insoluble ions

1. Hydroxide (OH^{1-}) and sulfides (S^{2-}) are insoluble except when the cation is an alkali metal, ammonia, or a heavy alkaline earth metal ions: Ca^{2+}, Ba^{2+}, and Sr^{2+}. (Recall the phrase “Come By Soon” to recall calcium, barium, and strontium.)
2. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), and oxide (O^{2-}) are insoluble except when the cation is an alkali metal, ammonia
3. If there is a conflict between the two guidelines, then the guideline listed first has priority. For example, the salts of insoluble ions become soluble when the cation is an alkali metal, ammonia (rule#1).

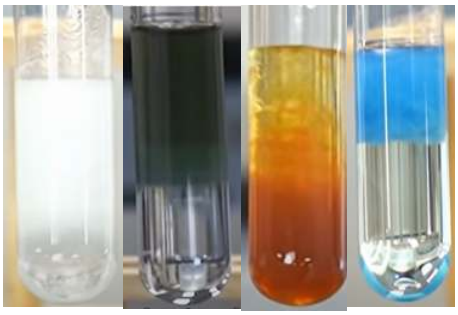


Figure 8.2.8: The precipitates of some insoluble ionic compounds formed by mixing the aqueous solution of appropriate soluble ionic compounds. The precipitates are from the left: white Calcium sulfate ($CaSO_4$), black Iron(II) hydroxide ($Fe(OH)_2$, brown Iron(III) hydroxide ($Fe(OH)_3$), and blue Copper(II) hydroxide ($Cu(OH)_2$). Source: https://youtu.be/jltLlzZ6FqU

Fig. 5.2.8 shows precipitates of some insoluble ionic compounds formed by mixing aqueous solutions of appropriate soluble ionic compounds. The precipitation can be predicted, as illustrated in Fig. 5.2.9. List the ions of the soluble ionic compounds and then cross-combine the cations of one with the anion of the other to make the potential products. If any of the potential products is an insoluble ionic compound, it precipitates out.

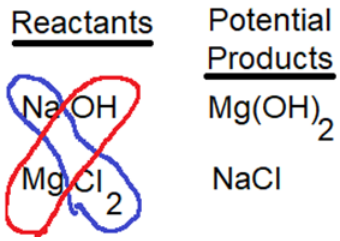


Figure 8.2.9: Cross-combine the cation-anion in the reactants. If any of the cross-combination is an insoluble salt, it will precipitate out, e.g: $\mathbf{NaOH(aq) + MgCl_2(aq) \rightarrow Mg(OH)_2(\,s)\downarrow + NaCl(aq)}$.

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8.3: Electrolytes

What is an electrolyte?

Electric current is defined as the movement of electric charges. The substances through which an electric current can flow are called electrical conductors, and the others are electrical nonconductors. Metals are electrical conductors because valence electrons of metal atoms can move around in a piece of metal. Ionic compounds are composed of cations and anions, but the ions in a solid can not move around. Therefore, solid ionic compounds are electrical nonconductors. Pure water does not have a sufficient concentration of ions in it and is an electrical nonconductor. The ionic compounds dissociate into ions when dissolved in water. The solution of ionic compounds in water is an electrical conductor because the ions can move around in the solution, as illustrated in Fig. 5.3.1.

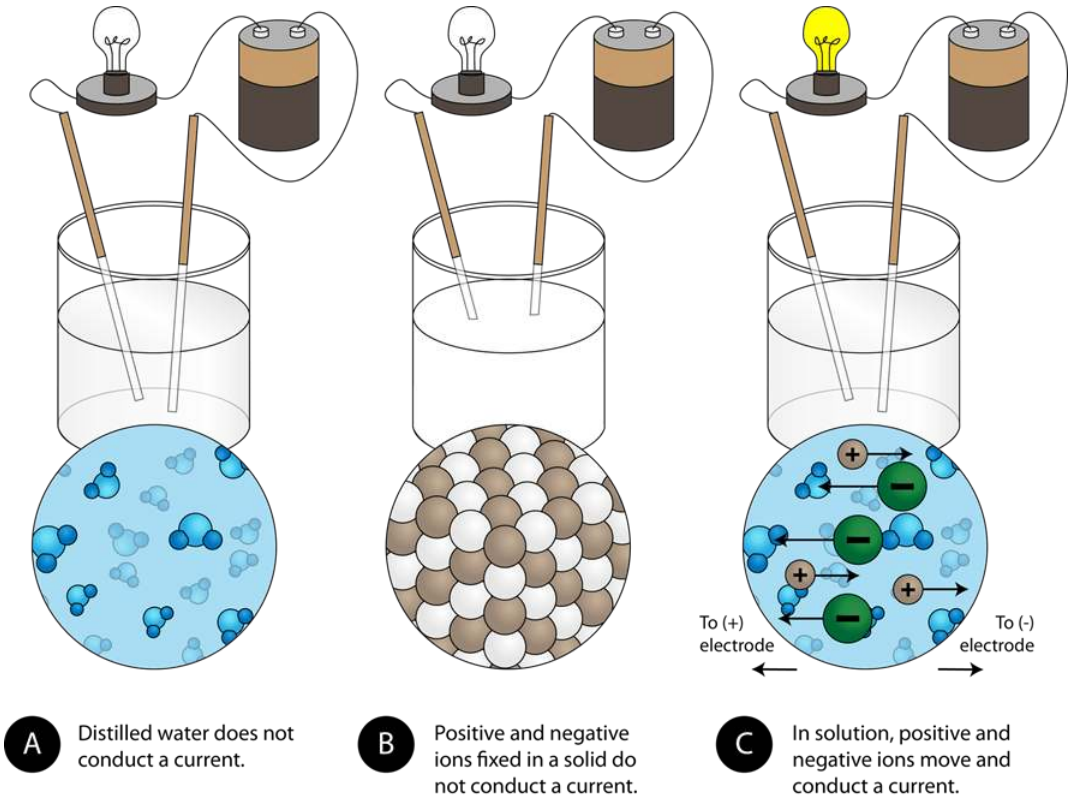


Figure **8.3.1**: Pure water (A) and solid ionic compounds (B) are electrical noncondutors, but the solution of ionic compounds in water is an electrical conductor. Source: https://www.hiclipart.com/free-trans...cmeih/download

> Substances that produce electrically conducting solution when dissolved in water (or in another polar solvent) are called **electrolytes**.

All ionic compounds, acids, and bases produce ions in water and are classified are electrolytes.

> Substances that produce an electrically nonconducting solution when dissolved in water are called **nonelectrolytes**.

Molecular compounds other than acids and bases, such as methanol, acetone, sugar, and glucose, remain neutral molecules when dissolved in water. The molecular solutes, other than acids and bases, are nonelectrolytes.

Strong and weak electrolytes

> Substances that almost 100% dissociate into ions when dissolved in water are **strong electrolytes**.
>
> 1. All ionic compounds that are soluble in water are strong electrolytes.
> 2. Strong acids are strong electrolytes.

3. Strong bases are ionic compounds and strong electrolytes.

A strong electrolyte does not mean that it is necessarily highly soluble in water. It means that the portion of the solute that dissolves, it also dissociates 100% into ions in water, e.g., all ionic compounds. The solubility $Ca(OH)_2$ is only 0.16 g $Ca(OH)_2$/100 g water at 20 ^oC, but all the dissolved $Ca(OH)_2$ dissociates into Ca^{2+} and OH^- ions.

Strong bases are hydroxides of alkali metals, i.e., LiOH, NaOH, KOH, RbOH, and CsOH, and hydroxides of heavy alkaline earth metals, i.e., $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$, which are strong electrolytes. Strong acids, i.e., HCl, HBr, HI, $HClO_4$, HNO_3, and H_2SO_4, are molecular compounds but are strong electrolytes because they dissociate almost 100% into ions when dissolved in water. For example, HCl almost wholly dissociates into ions when dissolved in water.

$$\mathrm{HCl(g) + H_2O(l) \rightarrow H_3O^{1+}(aq) + Cl^{1-}(aq)}$$

Substances that partially dissociate into ions when dissolved in water are **weak electrolytes**. Weak acids and weak bases are weak electrolytes.

Week acids and week bases, like acetic acid (CH_3COOH) and ammonia (NH_3), are soluble in water, but partially dissociate into ions. For example, if 1-mole acetic acid or 1-mole of ammonia is dissolved in 1 liter of water at room temperature, they establish the following equilibrium between dissolved molecules and dissociated ions:

$$\mathrm{CH_3COOH(l) \overset{Water}{\longrightarrow} CH_3COOH(aq) + H_2O(l) \rightleftarrows CH_3COO^{1-}(aq) + H_3O^{1+}(aq),}$$
$$\mathrm{NH_3(\,g) \overset{Water}{\longrightarrow} NH_3(aq) + H_2O(l) \rightleftarrows NH_4{}^{1+}(aq) + OH^{1-}(aq),}$$

where only about 0.4% of the dissolved molecules dissociate into ions, the remaining about 99.6% of molecules remain neutral. Weak acids and weak bases are weak electrolytes.

Fig. 5.3.2 illustrates the difference between nonelectrolytes, strong electrolytes, and weak electrolytes.

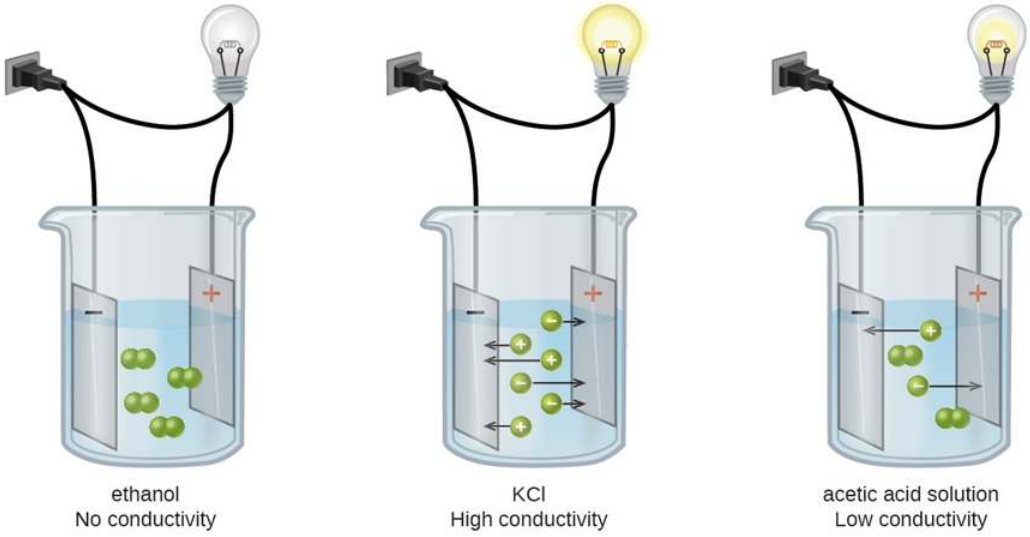


Figure **8.3.2**: Illustration of a nonelectrolyte that does not conduct electricity, a strong electrolyte that has high electrical conductivity, and a weak electrolyte that has low electrical conductivity. Source: Karishma50/ (https;//creativecommons.org/licences/by-sa/4.0)

Equivalent

The amount of molecules and atoms is usually measured in moles. Ionic compounds are composed of ions but are overall neutral because the +ve charge is balanced by the –ve charge. Therefore, the mole ratio of cations to anions is not always one to one. For example, NaCl has a one-to-one mole ratio of Na^+ and Cl^-, but $CaCl_2$ has a one-to-two ratio of Ca^{2+} and Cl^-. A new unit, called

equivalent (officially abbreviated as Equiv but commonly abbreviated as Eq), is introduced, to differentiate between a mole of ion and a mole of charge on the ion.

The *equivalent* is the amount of a substance needed to react with or supply one mole of hydrogen ions (H^+) in an acid-base reaction, or react with or supply one mole of electrons in a redox reaction. In other words, the number of equivalents of a given ion in a solution is equal to the number of moles of that ion multiplied by its valence.

$$1 \text{ mol } Na^+ = 1 \text{ Eq } Na^+, \text{ but } \quad 1 \text{ mol } Ca^{2+} = 2 \text{ Eq } Ca^{2+}, \text{ and } 1 \text{ mol } Al^{3+} = 3 \text{ Ea } Al^{3+}$$

Similarly,

$$1 \text{ mol } Cl^- = 1 \text{ Eq } Cl^-, \text{ but } \quad 1 \text{ mol } CO_3^{2-} = 2 \text{ Eq } CO_3^{2-} \text{ and } 1 \text{ mol } PO_4^{3-} = 3 \text{ Ea } PO_4^{3-}$$

The solutions of electrolytes are overall electrically neutral, i.e., the number of equivalents of cations is equal to the number of equivalents of anions in the solution.

For example, if 1 mole of NaCl is dissolved in water, there is 1 Eq of Na^+ ions and 1 Eq of Cl^- ions in the solution. If one mole of $CaCl_2$ is dissolved in the water there is 2 Eq of Ca^{2+} ions and 2 Eq of Cl^- ions in the solution. Similarly, if 1 mole of NaCl and 1 mole of $AlCl_3$ are dissolved in the water there is 1 Eq of Na^+ ions, 3 Eq of Al^{3+} ions, and 4 Eq of Cl^- ions to balance cations in the water.

Equality gives two conversion factors. For example, the equality 1 mol Ca^{2+} = 2 Eq Ca^{2+} gives the following two conversion factors:

$$\frac{1 \text{ mol } Ca^{2+}}{2 \text{ Eq } Ca^{2+}}$$

and

$$\frac{2 \text{ Ea } Ca^{2+}}{1 \text{ mol } Ca^{2+}}$$

The first conversion factor converts the given amount in equivalents to moles, and the second converts the given amount in moles to equivalents of the ion as explained in the following examples.

Example 8.3.1

a) Calculate mEq of Fe^{3+} in 0.0200 mol of Fe^{3+}? b) if chloride ion is the only anion in the solution, how many mEq of Cl^- are present in the solution?

Solution

a) Given 0.0200 mol Fe^{3+}. Desired mEq Fe^{3+}.

The equality: 1 mol Fe^{3+} = 3 Eq Fe^{3+} gives the conversion factor $\frac{3 \text{ Eq } Fe^{3+}}{1 \text{ mol } Fe^{3+}}$ that converts the given amount in moles to Eq of Fe^{3+}. Another equality: 1 Eq Fe^{3+} = 1000 mEq Fe^{3+} gives the conversion factor $\frac{1000 \text{ mEq } Fe^{3+}}{1 \text{ Eq } Fe^{3+}}$, that converts the Eq of Fe^{3+} to mEq of Fe^{3+}.

Calculations:

$$0.0200 \cancel{\text{ mol } Fe^{3+}} \times \frac{3 \cancel{\text{ Eq } Fe^{3+}}}{1 \cancel{\text{ mol } Fe^{3+}}} \times \frac{1000 \text{ mEq } Fe^{3+}}{1 \cancel{\text{ Eq } Fe^{3+}}} = 60 \text{ mEq } Fe^{3+}$$

Example 8.3.2

An intervenous saline solution contains 145 mEq/L of Na^+. How many moles of Na^+ are in 0.500 L of the solution?

Solution

a) Given: 145 mEq Na^+ /L solution and 0.500 L solution, Desired: ? mol Na^+

Conversion factors needed: The concentration in mEq/L is the first factor for L to mEq conversion, the equality 1 mEq Na^+ = 1 mmol Na^+ givens the second conversion needed for mEq to mmol conversion, and the equality 1000 mmol Na^+ = 1 mol Na^+ given the third conversion factor needed needed for mEq to mol conversion. The three conversion factors are applied one after the other in a single row in the following calculation:

$$0.500 \cancel{\text{ L solution}} \times \frac{145 \cancel{\text{ mEq Na}}}{1 \cancel{\text{ L solution}}} \times \frac{1 \cancel{\text{ mmol Na}^+}}{1 \cancel{\text{ mEq Na}^+}} \times \frac{1 \text{ mol Na}^+}{1000 \cancel{\text{ mmol Na}^+}} = 0.0725 \text{ mol Na}^+$$

Note how the units of the numerator in one fraction are canceled by the units of the denumerator of the following fraction leaving only the desired units uncancelled that become the units of the answer number.

Electrolytes in body fluids

Fig. 5.3.3 shows the electrolytes and their concentrations commonly found in body fluids. They play an essential role in cell and body functions. For example, sodium ions regulate the water content and play a role in electrical impulse transmission in the nervous system. Potassium ions play a role in maintaining a regular heartbeat and also play a part in electrical impulse transmission. Chloride ions are there to balance the charge. Carbonate ions are involved in maintaining the pH of the blood.

Concentrations of electrolytes in body fluids are not high enough to be reported in a mole or equivalent units. The electrolytes in the body fluids are usually reported in millimoles (mmol) or milliequivalent (mEq) units, where: **1000 mmol = 1 mol** and **1000 mEq = 1 Eq**.

The overall concentration of electrolytes in intravenous fluids given to patients is about the same as of electrolytes in the body fluids. For example, Ringer's lactate solution contains about: 130 mEq/L Na^+, 4 mEq/L K^+, 3 mEq/L Ca^{2+}, 109 mEq/L Cl^-, and 28 mEq/L lactate$^-$. Note that the overall +ve charge (130+4+3= 137 mEq/L) is equal to the overall –ve charge (109+28 = 137 mEq/L).

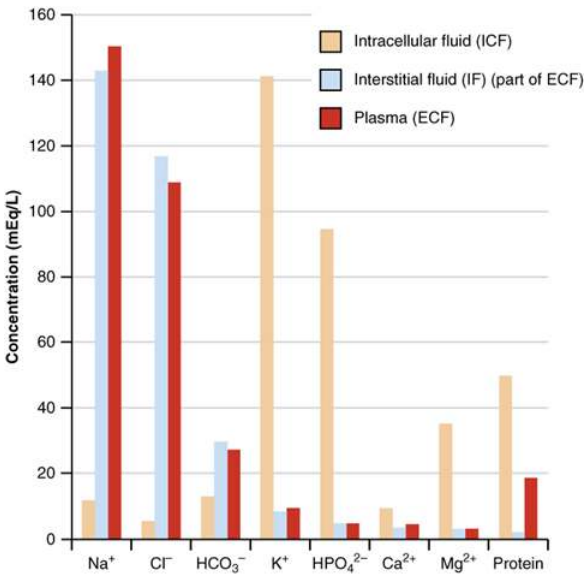


Figure **8.3.3**: Concentrations of electrolytes in body fluids. Source: OpenStax College / CC BY (https://creativecommons.org/licenses/by/3.0)

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8.4: Concentration of solutions

The concentration of a solution tells the amount of solute dissolved in a given amount of solution.

Making a solution of know concentration

A measured amount of solute is dissolved in enough solvent to make the desired volume of the solution, as illustrated in Fig. 5.4.1. The concentration of the solution can be expressed in different ways using mass, volume, or mole units, as explained in the following.

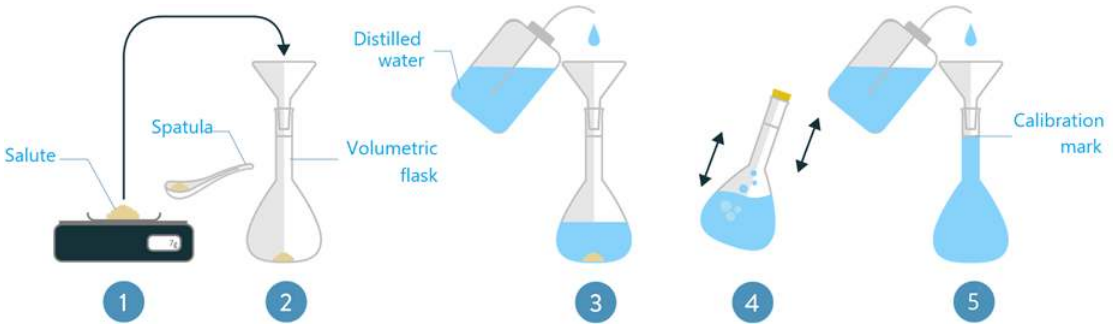


Figure **8.4.1**: Making an aqueous solution: 1) measure the mass of the solute on an analytical balance, 2) pour the solute into a volumetric flask of know volume, 3) add distilled water (or solvent) to more than half fill the flask, 4) stopper the flask and shake it to dissolve the solute, 5) add more water to fill the flask to the calibration mark –measure from the lowest point of the water meniscus, 6) stopper the flask and shake again to make a homogeneous solution. Source: modified from https://www.hiclipart.com/free-trans...cvcrq/download

Concentration in percent (%)

What is percent (%)

Percentage (%) is a number or ratio that represent a fraction of 100.

For example, 5% means 5:100, where 5 is the part, and 100 is the total. The percentage is calculated as a hundred times of part by total, i.e.,

$$\textbf{Percentage (\%)} = \frac{\textbf{part}}{\textbf{Total}} \times 100.$$

Example 8.4.1

A 50.0 g NaCl is dissolved in water to make a 500 g solution. What is the percentage of NaCl in the solution?

Solution

Given part = 50.0 g NaCl, and total = 500 g solution. Desired: %NaCl in the solution?

Formula: $\textbf{Percentage (\%)} = \frac{\textbf{part}}{\textbf{Total}} \times 100.$

Calculations: $\textbf{Percentage (\%)} = \frac{50.0 cancel\ g}{500 cancel\ g} \times 100 = 10.0\ \%\text{NaCl}$

The units cancel in the fraction calculation part, and a % sign is added to the answer to tell that it is a fraction out of a hundred.

Mass percent (m/m)% concentration

The mass percent concentration expresses the mass units of solute in a hundred mass units of the solution.

$$\text{Mass}(\%) = \frac{\text{mass of solute } (g)}{\text{mass of solute } (g) + \text{ mass of solvent } (g)} \times 100 = \frac{\text{mass of solute } (g)}{\text{mass of solution } (g)} \times 100$$

Note that the total is solute and solvent added together, i.e., solution.

Example 8.4.2

What is the mass % of NaOH in a solution prepared by dissolving 10.0 g NaOH in 100 g water?

Solution

Given solute = 10.0 g, and solvent = 100 g, Desired: Mass% NaOH?

Formula: $\text{Mass (\%)} = \frac{\text{mass of solute } (g)}{\text{mass of solute } (g) + \text{mass of solvent } (g)} \times 100$

Calculations: $\text{Mass (\%)} = \frac{10.0\ \text{gNaOH}}{(10.0\ \text{g} + 100\ \text{g})\ \text{solution}} \times 100 = 9.09\%\text{NaOH}$

Note that the mass% concentration and its reciprocal are two conversion factor: $\frac{\text{given } g \text{ solute}}{100 g \text{ solution}}$ and $\frac{100 g \text{ solution}}{\text{given g solute}}$

Example 8.4.3

Neosporin antibiotic is a 3.5% m/m neomycin solution. How many grams of neomycin are in 50 g of ointment?

Solution

Given: $3.5\%\ \text{neomycin} = \frac{3.5\ \text{g neomycin}}{100\ \text{g solution}}$, and Solution amount = 50 g, Desired: ? g neomycin

Calculations:

$$50\ \cancel{\text{g solution}} \times \frac{3.5\ \text{g neomycin}}{100\ \cancel{\text{g solution}}} = 1.8\ \text{g neomycin}.$$

Volume percent (v/v)% concentration

The volume percent concentration expresses the volume units of solute in a hundred volume units of the solution.

The mathematical form of the v/v % is:

$$\text{Volume (\%)} = \frac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100$$

Fig. 5.4.2 shows the volume percent concentration ranges of different classes of fragrances.

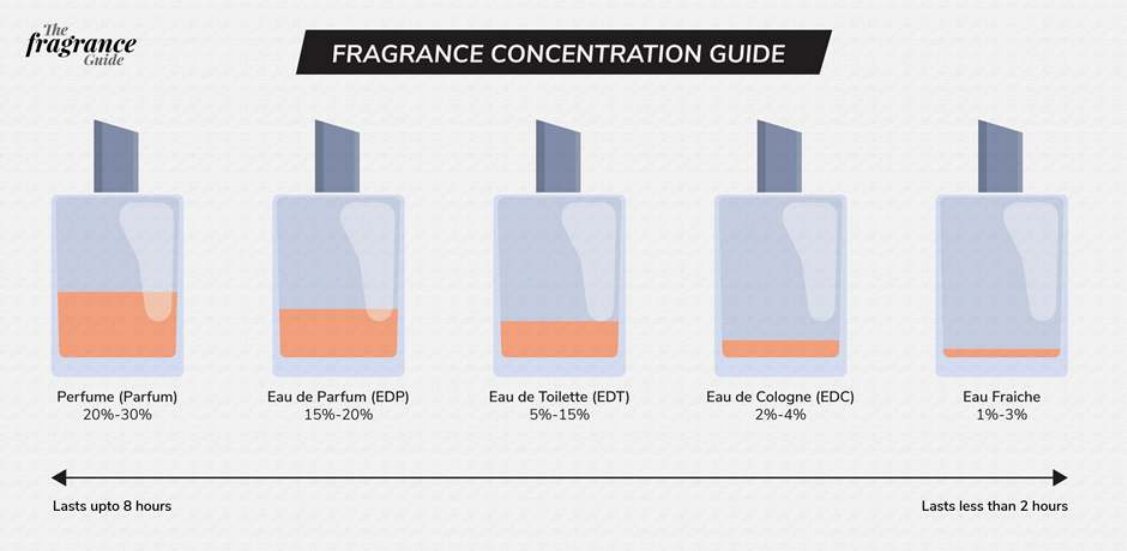


Figure 8.4.2: This info-graphic explains the differences between Parfums, Perfumes, Eau de Perfume, Eau de Parfum, Eau de Toilette, and Cologne. It also gives an approximate idea of how the concentration of Parfum oils vary as we move to lighter scents. Source: Nicole Smith / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

Example 8.4.4

What is the volume % of rose extract in a solution prepared by dissolving 14.0 mL rose extract in a solvent to make 200 mL of solution?

Solution

Given: Solute = 14.0 g, and solution = 200 g, Desired: Volume% rose solution?

Formula:

$$\text{Volume (\%)} = \frac{\text{volume of solute } (mL)}{\text{volume of solution } (mL)} \times 100$$

Calculations:

$$\text{Volume (\%)} = \frac{\text{14 mL rose extract}}{\text{200 mL solution}} \times 100 = \text{7.0\% rose solution}$$

The two conversion factors for v/v % concentration are:

$$\frac{\text{given mL solute}}{\text{100 mL solution}} \text{ , and } \frac{\text{100 mL solution}}{\text{given mL solute}}$$

Example 8.4.5

What is the volume of bromine (Br_2) in 250 mL of 4.8% v/v of Br_2 solution in carbon tetrachloride?

Solution

Given: Concentration 4.8% v/v bromine $= \frac{4.8\ mL\ \text{bromine}}{100\ mL\ \text{solution}}$, volume of solution = 250 mL, Desired: Volume of solute, i.e., ? mL bromine.

Calculations:

$$\text{250 mL solution} \times \frac{\text{4.8 mL bromine}}{\text{100 mL solution.}} = \text{12 mL bromine.}$$

Mass/volume percent (m/v)% concentration

The mass/volume percent concentration expresses the mass units of solute in a hundred volume units of solution.

Mathematical form of m/v % is:

$$\text{Mass/volume (\%)} = \frac{\text{mass of solute } (g)}{\text{volume of solution } (mL)} \times 100$$

Example 8.4.6

What is the mass/volume % of glucose solution prepared by dissolving 50 g glucose in enough water to make 1000 mL of solution?

Solution

Given: Solute = 50.0 g, and Solution = 1000 mL, Desired: Mass/volume % glucose solution?

Formula:

$$\text{Mass/volume (\%)} = \frac{\text{mass of solute } (g)}{\text{volume of solution } (mL)} \times 100$$

Calculations:

$$\frac{\text{Mass}}{\text{volume}}(\%) = \frac{\text{50 g glucose}}{\text{1000 mL solution}} \times 100 = \text{5.0\% glucose solution by } \frac{\text{m}}{\text{v}}.$$

The two conversion factors from ms/v % concentration are:

$$\frac{\text{given } g \text{ solute}}{\text{100 mL solution}} \quad \text{and} \quad \frac{\text{100 mL solution}}{\text{given g solute}}$$

Example 8.4.7

How many grams of clindamycin antibiotics are in a 45 mL capsule of the 1.0% (m/v) clindamycin?

Solution

Given: % m/v concentration: 1.08 % m/v clindamycin $= \frac{\text{1.0 g clindamycin}}{\text{100 mL solution}}$, and volume of solution = 45 mL, Desired: ? g clindamycin?

Calculations:

$$\text{45 mL solution} \times \frac{\text{1.0 g clindamycin}}{\text{100 mL solution}} = \text{4.5 g clindamycin.}$$

Parts per million (ppm) and parts per billion (ppb) concentration

Parts per million (ppm) is a number or ratio expressed as a fraction of a million (10^6).

For example, 2 ppm means $\frac{2}{1{,}000{,}000}$ or 2:1,000,000, where 2 is the part, and 1,000,000 is the total. The concentration in ppm is calculated as a million times of part by total, i.e.:

$$\text{Concentration in ppm} = \frac{part}{\text{Total}} \times 10^6$$

Parts per billion (ppb) is a number or ratio expressed as a fraction of billion (10^9).

That is:

$$\text{Concentration in ppb} = \frac{\text{part}}{\text{Total}} \times 10^9$$

Like percentage concentration, the ppm and ppb can be mass/mass (m/m), volume/volume (v/v) or mass/volume (m/v).

Example 8.4.8

EPA's action limit for copper is 1.3 mg/L in drinking water. What is this limit in ppm of copper m/v in the drinking water?

Solution

Given: 1.3 mg copper in 1L solution, Desired: ? ppm m/v of Copper in water

Formula: $\text{Concentration in ppm} = \frac{\text{solute(g)}}{\text{solution(mL)}} \times 10^6$

Calculations: First, convert the given units of mass and volume into the corresponding units that the formula takes, then plug the values in the formula and calculate.

$$\text{Solute} = 1.3 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.0013 \text{ g}$$

$$\text{Solution} = 1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1000 \text{ mL}$$

$$\text{Concentration in ppm} = \frac{0.0013 \text{ g}}{1000 \text{ mL}} \times 10^6 = 1.3 \text{ ppm copper } v/\text{m}$$

Example 8.4.9

EPA's action limit for lead is 0.015 mg/L in drinking water. What is this limit in ppb of lead m/v in the drinking water?

Solution

Given: 0.015 mg in 1L solution, Desired: ? ppb m/v of Lead in water

Formula: $\text{Concentration in ppb} = \frac{\text{solute}(g)}{\text{solution(mL)}} \times 10^9$

Calculations: First, convert the given units of mass and volume into the corresponding units that the formula takes, then plug the values in the formula and calculate.

$$\text{Solute} = 0.015 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.000015 \text{ g}$$

$$\text{Solution} = 1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1000 \text{ mL}$$

$$\text{Concentration in ppb} = \frac{0.000015 \text{ g}}{1000 \text{ mL}} \times 10^9 = 15 \text{ ppb lead v/m}$$

Molarity

Molarity (M) expresses the moles of solute in a liter of solution.

The most common solution concentration unit used in chemistry is molarity (M):

$$\text{Molarity } (M) = \frac{n \text{ (moles of solute)}}{V \text{ (Litters of solution)}}$$

Example 8.4.10

What is the molarity (M) of a solution prepared by dissolving 50.0 g NaOH in enough water to make 250 mL solution?

Solution

Given: Solute = 50.0 g NaOH, Volume of solution = 250 mL, Desired: ? M NaOH solution?

Formula: $\text{Molarity } (M) = \frac{n \text{ (moles of solute)}}{V \text{ (Litters of solution)}}$

Calculations: First, convert the given units of mass and volume into the corresponding units that the formula takes, then plug the values in the formula and calculate.

$$\text{Solute} = 50.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 1.25 \text{ mol NaOH}$$

$$\text{Solution} = 250 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.250 \text{ L}$$

$$\text{Molarity } (M) = \frac{1.25 \text{ mol NaOH}}{0.250 \text{ L solution}} = 5.00 \text{ M NaOH}$$

The two conversion factor from molarity are the following:

$$\frac{n \text{ (moles of solute)}}{V \text{ (Litters of solution)}} \quad \text{and} \quad \frac{V \text{ (Litters of solution)}}{n \text{ (moles of solute)}}$$

Example 8.4.11

How many litters of 0.211 M HCl solution are needed to provide 0.400 mol of HCl?

Solution

Given: amount of solute = 0.400 mol HCl, Concentration of solute = 0.211M = $\frac{0.211 \text{ mol HCl}}{1L \text{ solution}}$

Calculations:

$$\text{Liters of solution needed } = 0.400 \text{ mol HCl} \times \frac{1 \text{ L soluton}}{0.211 \text{ mol HCl}} = 1.90 \text{ L solution}$$

Example 8.4.12

A 2.50 L of 1.12 M NaOH solution contains how many moles of NaOH?

Solution

Given: Volume of solution = 2.50 L solution, concentration of solution = $\text{1.12 M NaOH} = \frac{\text{1.12 mol NaOH}}{\text{1 L solution}}$, Desired: ? moles of NaOH?

Calculations:

$$\text{Moles of NaOH in the solution } = 2.50 \text{ L solution} \times \frac{1.12 \text{ mol NaOH}}{1 \text{ L solution}} = 2.80 \text{ mol NaOH}$$

Dilution of solutions

Dilution of a solution is the addition of a solvent to decrease the solute concentration of the solute in the solution.

The product of concentration (C) and volume (V) is the amount of solute, i.e.,

$$\text{Amount of solute } = C \text{ in } \frac{\text{amount of solute}}{\text{volume of solution}} \times V \text{ in volume of solution.}$$

The amount of solute does not change by adding solvent. Therefore, the product of concentration and volume, i.e., CV, which is the amount of solute, is a constant, i.e.,

$$C_1V_1 = C_2V_2 = \text{ amount of solute}$$

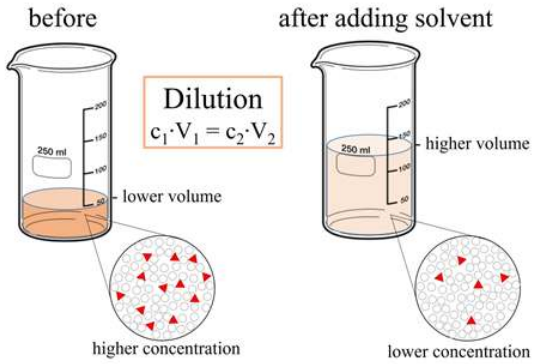


Figure **8.4.3**: This image illustrates that when more solvent is mixed with the solution, the amount of solute remains the same, but its concentration decreases. Source: Theislikerice / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

Fig. 5.4.3 shows that if the initial concentration is C_1, the initial volume is V_1, and after dilution, the final concentration is C_2, the final volume is V_2, then $C_1V_1 = C_2V_2$ = amount of solute that is constant. If three of the four variables in this equation are known, the missing one can be calculated, as explained in the following example.

Caution

Keep in mind that the concentrations and volumes should be in the same units on both sides of the equation: $C_1V_1 = C_2V_2$. If they are not in the same units, convert them to the same units before plunging them in the formula.

Example 8.4.13

how much volume of 11.3 M HCl is needed to prepare 250 mL of 2.00 M HCl?

Solution

Given: C_1 = 11.3 M HCl, C_2 = 2.00 M HCl, V_2 = 250 mL solution, Desired V_1 = ?

Formula: $C_1V_1 = C_2V_2$, rearrange it to isolate the desired parameter: $V_1 = \frac{C_2V_2}{C_1}$

Calculations:

$$V_1 = \frac{C_2V_2}{C_1} = \frac{\text{2.00 M HCl} \times \text{250 mL solution}}{\text{11.3 M HCl}} = \text{44.2 mL solution}$$

Example 8.4.14

what is the molarity of the NaOH solution prepared by diluting 100 mL of 0.521 M NaOH solution to 500 mL?

Solution

Given C_1 = 0.521 M NaOH, V_1 = 100 mL solution, V_2 = 500 mL solution, Desired: Concentration of the final solution C_2 = ? M NaOH

Formula: $C_1V_1 = C_2V_2$, rearrange to isolate the desired parameter: $C_2 = \frac{C_1V_1}{V_2}$

Calculations:

$$C_2 = \frac{C_1V_1}{V_2} = \frac{\text{0.521 M NaOH} \times \text{100 mL NaOH}}{\text{500 mL NaOH}} = \text{0.104 M NaOH}$$

Example 8.4.15

Dopamine is administered intravenously to a patient to increase blood pressure. How many milliliters (mL) of a 4.0% (m/v) dopamine solution is needed to prepare 250 mL of a 0.030% m/v) solution?

Solution

Given: C_1 = 4.0% (m/v), C_2 = 0.030% (m/v), V_2 = 250 mL solution, Desired V_1= ?

Formula: $C_1V_1 = C_2V_2$, rearrange to isolate the desired parameter: $V_1 = \frac{C_2V_2}{C_1}$

Calculations:

$$V_1 = \frac{C_2V_2}{C_1} = \frac{\text{0.030\%} \times \text{250 mL solution}}{\text{4.0\%}} = \text{5.0 mL of solution}$$

Logarithmic dilution

Take a unit volume of a given solution and add enough solvent to increase the volume of the solution 10 times for a logarithmic diluiton.

A logarithmic dilution is ten times dilution, i.e., proven by the following formula:

$$C_2 = \frac{C_1V_1}{V_2} = \frac{\text{1 mL} \times C_1}{\text{10 mL}} = 0.1 \times C_1$$

Repeating the above step with the diluted solution results in 10x10 = 100-time dilution, and repeating third-time results in 10x10x10 = 1000-time dilution. This dilution of 10 times in each step is called logarithmic dilution. Fig. 5.4.4 shows that five steps of logarithmic dilution on a 10% initial solution results in a concentration of 10 ppm in the final solution.

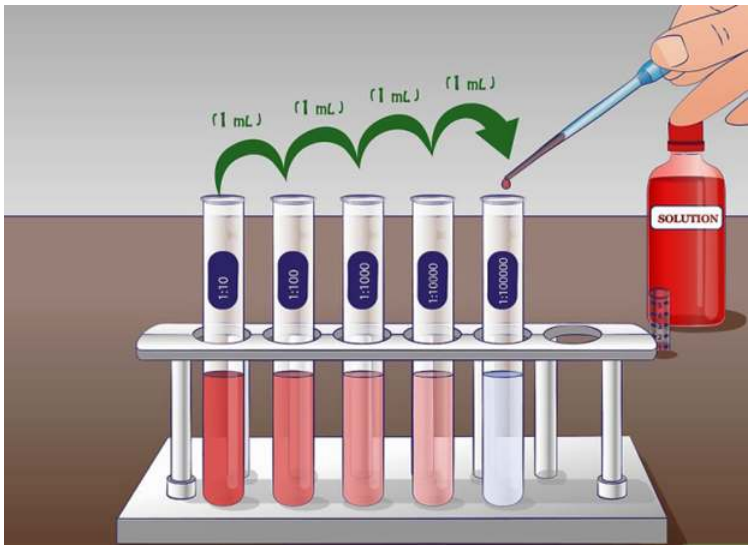


Figure 8.4.4: Logarithmic dilution: five steps of logarithmic dilution on a 10% initial solution results in a concentration of 10 ppm of the final solution. Source: Grasso Luigi / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

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8.5: Osmosis

Semipermeable membranes surround living cells and organelles in the cells. The semipermeable membranes allow water and small molecules but do not allow the passage of large molecules and ions.

> Osmosis is the passage of water and small molecules across a semipermeable membrane with a net flow from a less concentrated solution to a more concentrated solution.

Osmosis helps in the absorption, retention, and flow of water, nutrients, and other molecules required in the biological systems. Fig. 5.5.1 illustrates the process of osmosis.

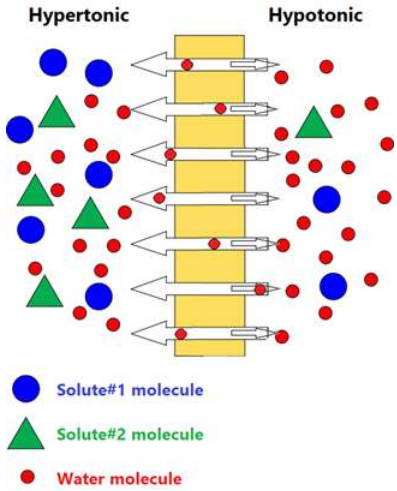


Figure **8.5.1**: Illustration of osmosis. Osmosis is the passage of water and small molecules through a semipermeable membrane with a net flow from low solute concentration to high solute concentration. The larger molecules and ions cannot pass the semipermeable membrane.

Osmotic pressure

Osmosis causes net water flow from the less concentrated to the more concentrated solution across the semipermeable membrane. Consequently, the water level rises in the less concentrated solution compartment, as illustrated in Fig. 5.5.2. The difference in the height of water increases and applies pressure, pumping water back to the more concentrated side until the flow of water is equal on the two sides.

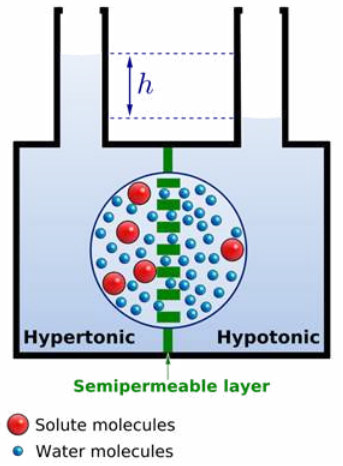


Figure **8.5.2**: Osmotic pressure is the pressure, due to the difference in the height of water in this example, that prevents the excess flow of water from less concentrated to more concentrated solution side across the semipermeable membrane that separates the two solutions. Source: WYassineMrabetTalk✉ This W3C-unspecified vector image was created with Inkscape. / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

The pressure that prevents additional water flow to the more concentrated solution side of the semipermeable membrane is called osmotic pressure.

The osmotic pressure is proportional to the overall concentration of the solute particles. For example, 0.1 molar NaCl has osmotic pressure about twice that of 0.1 molar glucose because each mole of glucose adds one mole of solute particles, while each mole of NaCl produces two moles of particles, i.e., one-mole Na^+ and one-mole Cl^- ions in the solution.

Reverse Osmosis

Reverse osmosis is the net flow of water to the less concentrated or pure water across the semipermeable membrane by applying external pressure more than the osmotic pressure on the more concentrated solution side.

Reverse osmosis is the net flow of water to the less concentrated or pure water across the semipermeable membrane by applying external pressure more than the osmotic pressure. Note that solvent flow in reverse osmosis driven by external pressure is the opposite of regular osmosis. Reverse osmosis is used to produce drinking water from seawater sources, as illustrated in Fig. 5.5.3.

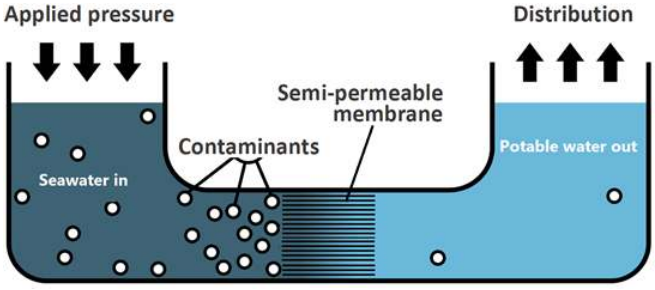


Figure **8.5.3**: Illustration of reverse osmosis –used to produce drinking water from a seawater source. Source: Colby Fisher / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

Isotonic, hypertonic, and hypotonic solutions

Cell membranes are semipermeable membranes that separate intracellular and extracellular fluids. The concentration difference across the membrane and the resulting osmotic pressure plays an essential role in cell functions. Intravenous solutions injected into patients must have the same osmotic pressure as the body fluids.

Solutions with the same solute particle concentration and osmotic pressure are called **isotonic**. If the two solutions across a semipermeable membrane do not have the same solute particle concentration, the solution with higher solute particle concentration and higher osmotic pressure is **hypertonic**, and the other has lower solute particle concentration and lower osmotic pressure is **hypotonic**.

Remember that hyper- means more and hypo-means less, concerning solute particle concentration in the case of osmosis.

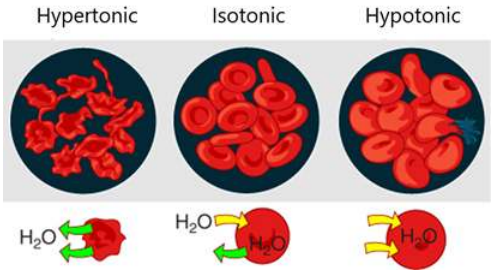


Figure **8.5.4**: A hypertonic solution has a solute concentration higher than another solution. An isotonic solution has a solute concentration equal to another solution. A hypotonic solution has a solute concentration lower than another solution. Source: OpenStax / CC BY (https://creativecommons.org/licenses/by/3.0)

Cells placed in an external solution may retain their size, shrink, or swell depending on the relative osmotic pressure of fluid inside and outside of the cell, as illustrated in Fig. 5.5.4. For example, red blood cells placed in an isotonic solution retain their size

because the flow of water into and out of the cell is the same.

- Typical isotonic solutions are 0.9% m/v NaCl solution in water or 5% m/v glucose solution in water.
- Red blood cells placed in a hypertonic solution shrink in size due to more flow of water out than into the cell –a process called **crenation**.
- Red blood cells placed in a hypotonic solution swell and burst due to more water flow into than out of the cells –a process called **hemolysis**.

A similar situation happens in plant cells that are placed in different environments concerning osmotic pressure, as illustrated In Fig. 5.5.5.

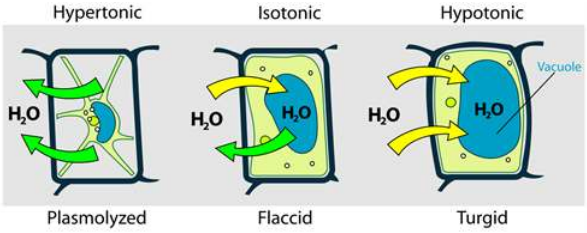


Figure 8.5.5: Plant cells under different environments concerning osmotic pressure. source: LadyofHats / Public domain

Dialysis

Dialysis separates colloids from water, dissolved ions, and molecules of small dimention

Dialysis is similar to osmosis with the difference that in dialysis water, small molecules and ions can pass through a dialyzing membrane leaving behind collide particles like proteins and starch molecules, as illustrated in Fig. 5.5.6.

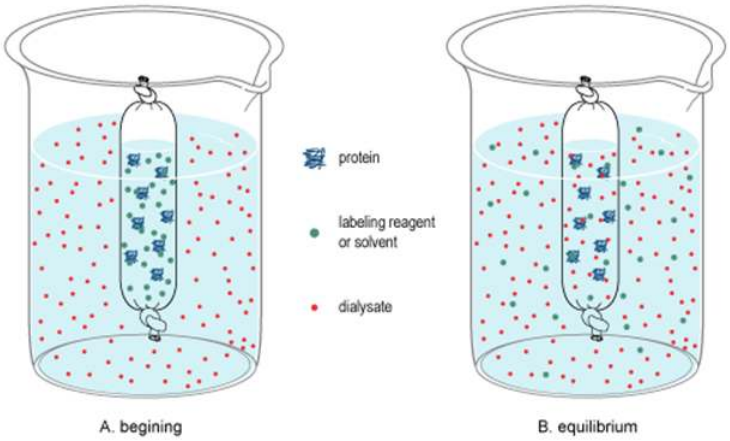


Figure 8.5.6: Dialysis separates colloidal particles like protein and starch from water, small molecules, and ions. Source: Potcherboy at English Wikipedia / CC BY (https://creativecommons.org/licenses/by/3.0)

Role of dialysis in the human body

Kidneys filter the blood by dialysis process. There are over a million tubular structures, called nephrons, in the kidney surrounded by dialyzing membranes. The nephrons filter the water, small molecules like glucose, amino acids, urea, and ions from the blood. Useful products and most of the water reabsorb later on, but urea and other waste products excrete through urine, as illustrated in Fig. 5.5.7.

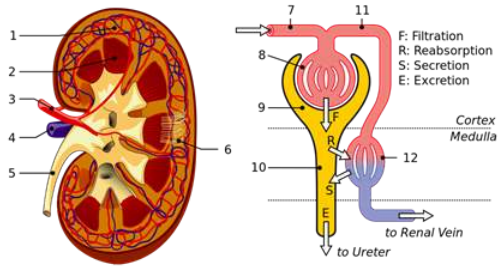


Figure **8.5.7**: Schematics of dialysis for blood cleaning through kidney and nephron. 1: Renal cortex. 2: Medulla. 3: Renal artery. 4: Renal vein. 5: Ureter. 6: Nephrons. 7: Afferent arteriole. 8: Glomerulus. 9: Bowman's capsule. 10: Tubuli and loop of Henle. 11: Efferent arteriole. 12: Peritubular capillaries. Source: File:Physiology_of_Nephron.svg: Madhero88File:KidneyStructures_PioM.svg: Piotr Michał Jaworski; PioM EN DE PLderivative work: Daniel Sachse (Antares42) / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

Hemodialysis

Hemodialysis is used to extract urea and other waste products from the blood when a person's kidney fails to remove them, as illustrated in Fig. 5.5.8. A hemodialysis system is a kind of artificial kidney in which the blood flows through long cellophane tubes placed in an isotonic solution containing NaCl, KCl, $NaHCO_3$, and glucose. Cellophane is a dialyzing membrane that does not let proteins, other large molecules, and blood pass through it, but urea excretes.

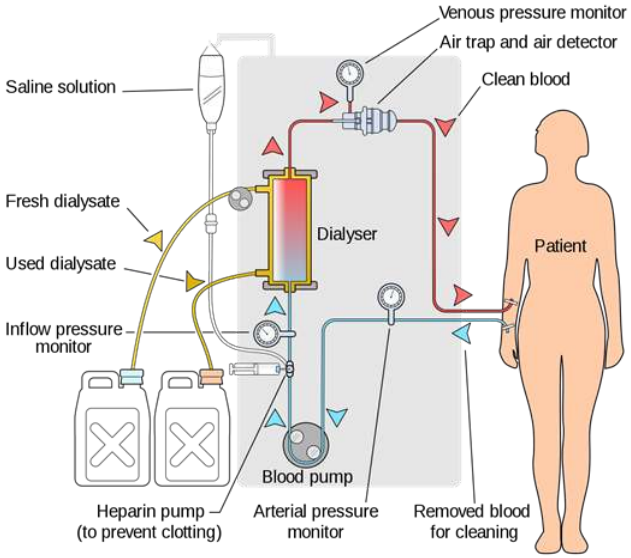


Figure **8.5.8**: Simplified hemodialysis circuit. Source: GYassineMrabetTalk✉ This W3C-unspecified vector image was created with Inkscape. / CC BY (https://creativecommons.org/licenses/by/3.0)

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CHAPTER OVERVIEW

9: Acids and Bases

9.1: Acids and Bases Definitions
9.2: Acid and Base Strength
9.3: Acid Dissociation Constants
9.4: Water as Both an Acid and a Base
9.5: Measuring Acidity in Aqueous Solutions- The pH Scale
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9.7: Acid-base equilibrium
9.8: Shifting Equilibria - Le Chatelier's Principle
9.9: Reactions of Acids and Bases
9.10: Acids and Bases in Industry and in Daily Life
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9.1: Acids and Bases Definitions

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 hydrogen ions, H^+, in solution and a base produces hydroxide ions, 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; 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.

$$\mathrm{HCl\,(aq)} \rightarrow \mathrm{H^+\,(aq) + Cl^-\,(aq)} \tag{9.1.1}$$

In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chloride (\Cl^{-}\)) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$\mathrm{HCl\,(aq) + H_2O(\ell)} \rightarrow \mathrm{H_3O^+\,(aq) + Cl^-\,(aq)} \tag{9.1.2}$$

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:

$$\mathrm{NaOH\,(aq)} \rightarrow \mathrm{Na^+\,(aq) + OH^-\,(aq)} \tag{9.1.3}$$

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

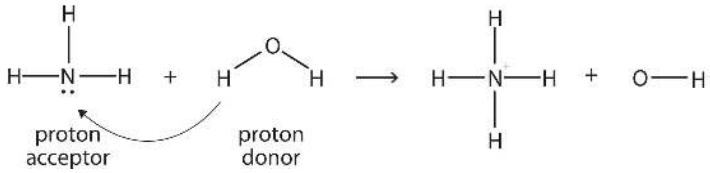
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

> *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:

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{9.1.4}$$

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:



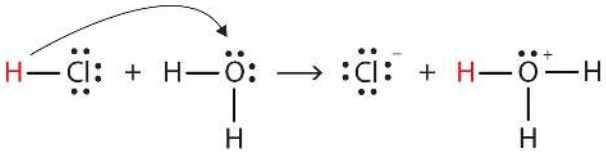
Because the water molecule *donates* a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which *accepts* the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

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.

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:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq)\ Cl^-(aq) + H_3O^+(aq) \tag{9.1.5}$$

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; the 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.

Note: Acid and Base Definitions

- 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 9.1.1

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 9.1.1

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

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \tag{9.1.6}$$

Answer

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

? Exercise 9.1.2

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer

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

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

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:

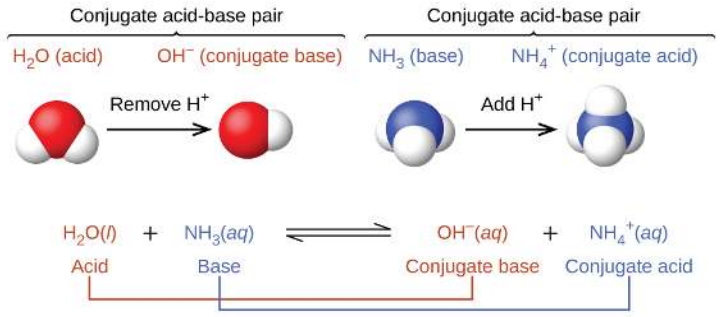
$$HPO_4^{2-}\,(aq) + H_2O\,(l) \rightarrow H_2PO_4^- + OH^-\,(aq)$$

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

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



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $\boldsymbol{NH_4^+/NH_3}$ and $\boldsymbol{H_2O/OH^-}$.

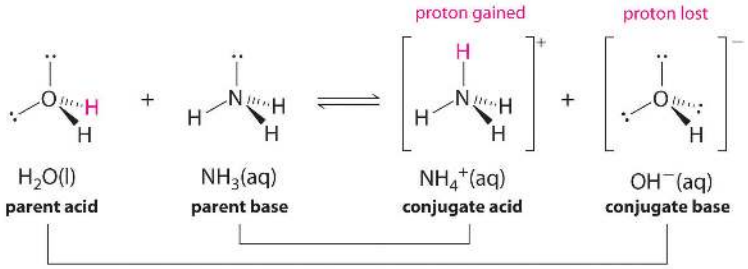


Figure 9.1.1. The pairing of parent acids and bases with conjugate acids and bases.

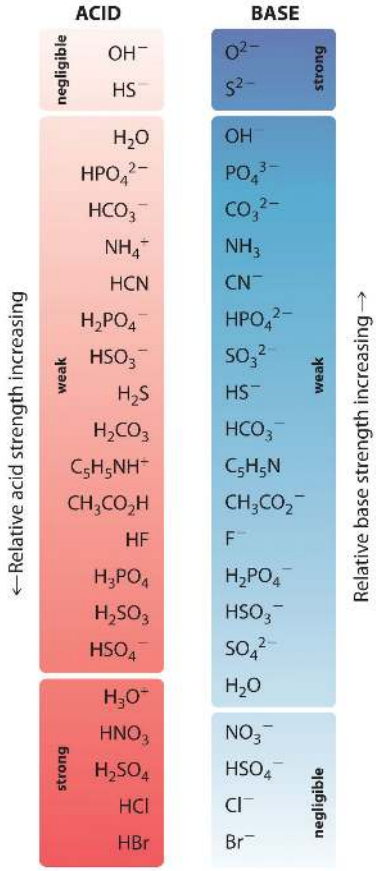


Figure 9.1.2: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

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Example 9.1.2

Identify the conjugate acid-base pairs in this equilibrium.

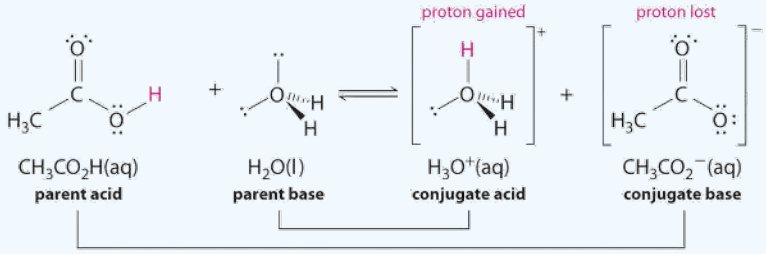
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

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 9.1.3

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 9.1.3

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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9.2: Acid and Base Strength

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.

Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider $\mathbf{HCl(aq)}$. When $\mathbf{HCl}$ is dissolved in $\mathbf{H_2O}$, it completely **dissociates** (separates) into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$\mathbf{HCl \xrightarrow{100\%} H^+(aq) + Cl^-(aq)} \tag{9.2.1}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq) \tag{9.2.2}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \tag{9.2.3}$$

As it turns out, there are very few strong acids, which are given in Table 9.2.1. 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.*

Figure 9.2.1: Some of the common strong acids and bases are listed here.

Strong Acids		Strong Bases	
$\mathbf{HClO_4}$	perchloric acid	$\mathbf{LiOH}$	lithium hydroxide
$\mathbf{HCl}$	hydrochloric acid	$\mathbf{NaOH}$	sodium hydroxide
$\mathbf{HBr}$	hydrobromic acid	$\mathbf{KOH}$	potassium hydroxide
$\mathbf{HI}$	hydroiodic acid	$\mathbf{Ca(OH)_2}$	calcium hydroxide
$\mathbf{HNO_3}$	nitric acid	$\mathbf{Sr(OH)_2}$	strontium hydroxide
$\mathbf{H_2SO_4}$	sulfuric acid	$\mathbf{Ba(OH)_2}$	barium hydroxide

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 9.2.1); 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 9.2.1: 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 **9.2.1**, it is a strong acid.

b. Because $Mg(OH)_2$ is listed in Table **9.2.1**, 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 9.2.1

Identify each acid or base as strong or weak.

a. **RbOH**

b. **HNO_2**

Answer

a. strong base

b. weak acid

Example 9.2.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

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

Because $Ca(OH)_2$ is listed in Table **9.2.1**, this reaction proceeds 100% to products.

Exercise 9.2.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer a

The reaction is as follows:

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

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

Looking Closer: Household Acids and Bases

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

One of the more familiar household bases is ammonia ($\mathrm{NH_3}$), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$\mathrm{NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)} \tag{9.2.4}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 9.2.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

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

Chemical Equilibrium in Weak Acids and Bases

Ionization of weak acids or bases are reversible reactions, which means the forward and reverse reactions occur and eventually reach equilbrium. For example, the ionization of the weak acid $\mathbf{HC_2H_3O_2\,(aq)}$ is as follows:

$$\mathbf{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{9.2.5}$$

The reverse process also begins to occur:

$$\mathbf{H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell)} \tag{9.2.6}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$\mathbf{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{9.2.7}$$

The $\rightleftharpoons$ implies that both the forward and reverse reactions are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

Example 9.2.3: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HNO_2(aq)$
b. $C_5H_5N(aq)$

Solution

a. $HNO_2(aq) + H_2O(\ell) \leftrightarrows NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \leftrightarrows C_5H_5NH^+(aq) + OH^-(aq)$

? Exercise 9.2.3

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

Answer

a. $HF(aq) + H_2O(\ell) \leftrightarrows F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

Strengths of Conjugate Acid and Base Pairs

The extent to which an acid, **HA**, donates protons to water molecules depends on the strength of the conjugate base, $\mathbf{A^-}$, of the acid. If $\mathbf{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathbf{A^-}$. Thus there is relatively little $\mathbf{A^-}$ and $\mathbf{H_3O^+}$ in solution, and the acid, **HA**, is weak. If $\mathbf{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathbf{A^-}$ and $\mathbf{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure **9.2.2**).

The first six acids in Figure **9.2.2** are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure **9.2.2** form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and non-ionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure **9.2.2** exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

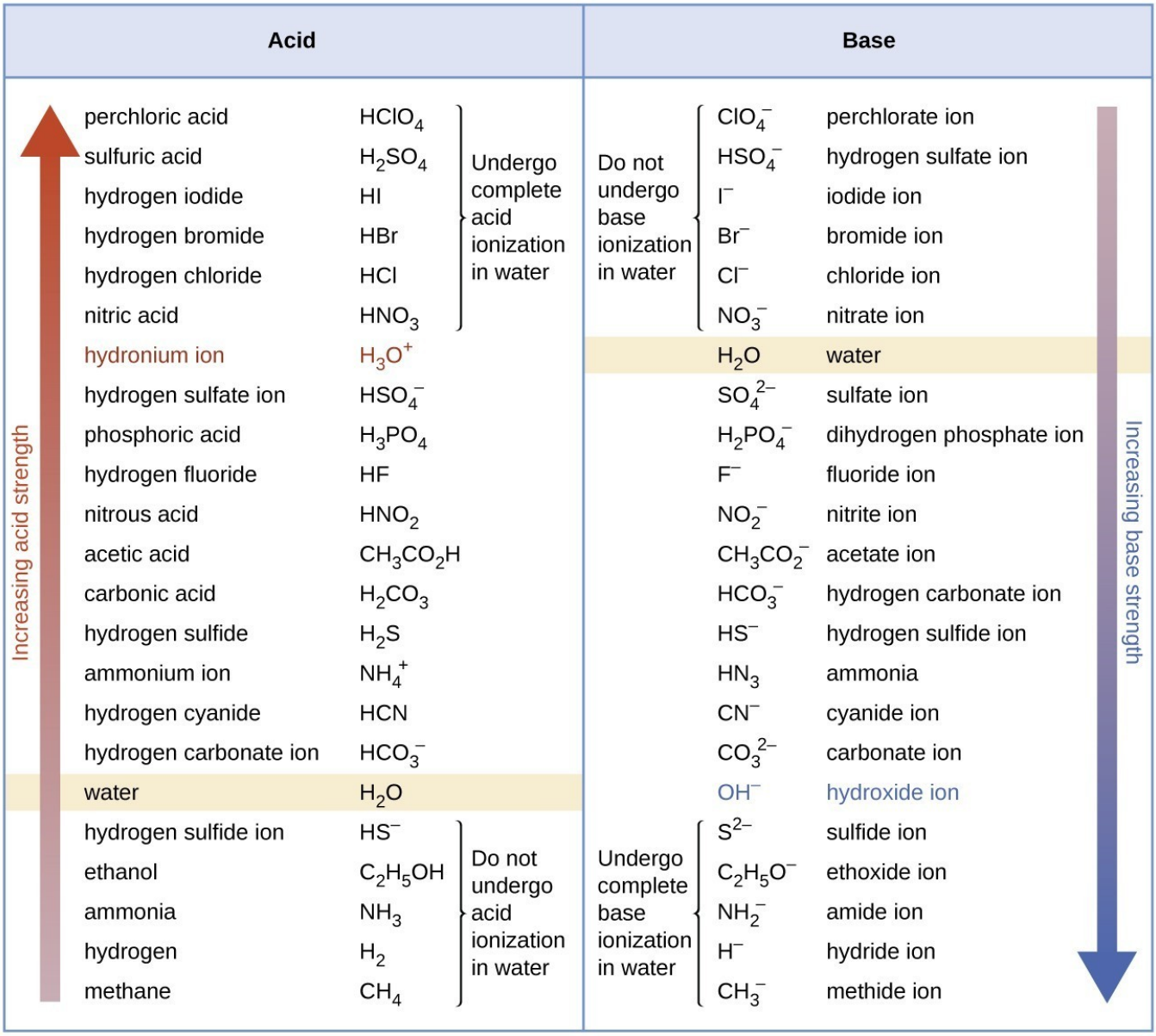


Figure **9.2.2**: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure **9.2.2**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Key Takeaways

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

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9.3: Acid Dissociation Constants

Learning Objectives

- Write the acid dissociation constant (K_a) expression.
- Determine the relative strength of an acid using the (K_a) value.

The ionization for a general weak acid, **HA**, can be written as follows:

$$\mathrm{HA}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the *equilibrium constant* for the ionization of an acid.

$$K_a = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

The acid ionization represents the fraction of the original acid that has been *ionized* in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially **100%** ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table **9.3.1**: Acid Ionization Constants at **25°C**

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$\mathrm{H_2SO_4 \rightleftharpoons H^+ + HSO_4^-}$ $\mathrm{HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}}$	very large 1.3×10^{-2}
Hydrofluoric acid	$\mathrm{HF \rightleftharpoons H^+ + F^-}$	7.1×10^{-4}
Nitrous acid	$\mathrm{HNO_2 \rightleftharpoons H^+ + NO_2^-}$	4.5×10^{-4}
Benzoic acid	$\mathrm{C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-}$	6.5×10^{-5}
Acetic acid	$\mathrm{CH_3COOH \rightleftharpoons H^+ + CH_3COO^-}$	1.8×10^{-5}
Carbonic acid	$\mathrm{H_2CO_3 \rightleftharpoons H^+ + HCO_3^-}$ $\mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

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9.4: Water as Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.
- Define and use the ion product constant for water, K_w, to calculate concentrations of H_3O^+ and OH^- in aqueous solutions.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$HCl + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{9.4.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{9.4.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{9.4.3}$$

This process is called the **autoionization of water** (Figure 9.4.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

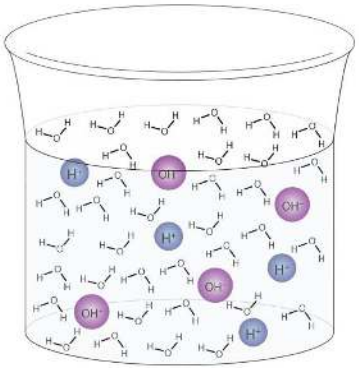


Figure 9.4.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 9.4.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

? Exercise 9.4.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Dissociation of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some $\mathbf{H_2O}$ molecules are acting as acids, and other $\mathbf{H_2O}$ molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{9.4.4}$$

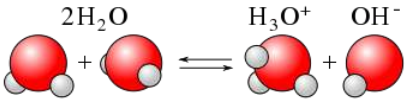


Figure **9.4.2**: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{9.4.5}$$

We often use the simplified form of the reaction:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_w = [H^+][OH^-]$$

The **ion-product constant for water (K_w)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*. To find the molarity of each ion, the square root of K_w is taken.

$$[H^+] = [OH^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[H^+]\times[OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$ is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This increases the concentration of H^+ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by

$$\mathrm{H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)}$$

$$\mathrm{HCl\,(g) \longrightarrow H^+\,(aq) + Cl^-\,(aq)}$$

is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

The increase in concentration of the OH^- ions will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$ is greater than $[OH^-]$.
- For basic solutions, [OH−] is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+] = [OH-] = 1.0\times10^{-7}$M

This means that if you know $[\mathrm{H^+}]$ for a solution, you can calculate what $[\mathrm{OH^-}]$) has to be for the product to equal $\mathbf{1.0 \times 10^{-14}}$, or if you know $[\mathrm{OH^-}]$), you can calculate $[\mathrm{H^+}]$. 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.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{9.4.6}$$

Example 9.4.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

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

Known

- [HCl] = 2.0×10^{-3} M
- Kw = 1.0×10^{-14}

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\,M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\,M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

? Exercise 9.4.2

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-] = 0.001M$ or $1 \times 10^{-3}M$; $[H^+]=1\times10^{-11}M$.

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid
3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

[SIDE NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.]

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9.5: Measuring Acidity in Aqueous Solutions- The pH Scale

Learning Objectives

- Define the pH scale and use it to describe acids and bases.
- Calculate the pH of a solution from $[H_3O^+]$ and $[OH^-]$.

Knowing the amount of acid and base in solutions is extremely important for a wide variety of applications ranging from brewing beer or wine to studying the effects of ocean acidification to health and medicine. Scientists are good at calculating and measuring the concentration of hydronium in a solution, however, there is a more convenient way to make comparisons between solutions – *the pH scale*.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure **9.5.1** 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.

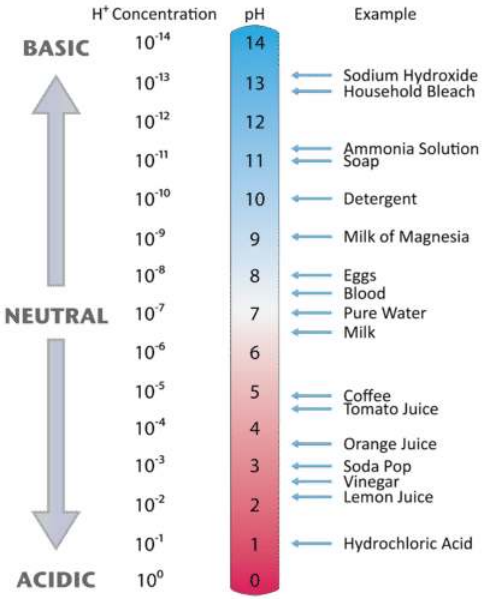


Figure **9.5.1**: The relationaship between $[H^+]$ and pH *values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \(\PageIndex{1}.

Table **9.5.1**: Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

Example 9.5.1

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

$pH = - \log [H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. $pH = - \log [1 \times 10^{-3}] = 3.0$ (1 decimal place since 1 has 1 significant figure)
b. $pH = - \log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures)
c. $pH = - \log [4.7 \times 10^{-9}] = 8.33$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

Exercise 9.5.1

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Figure **9.5.2** lists the pH of several common solutions. The most *acid*ic among the listed solutions is 1 M HCl with the lowest pH value (0.0): battery acid is the next most acidic solution with a pH value of 0.3. The most *basic* is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

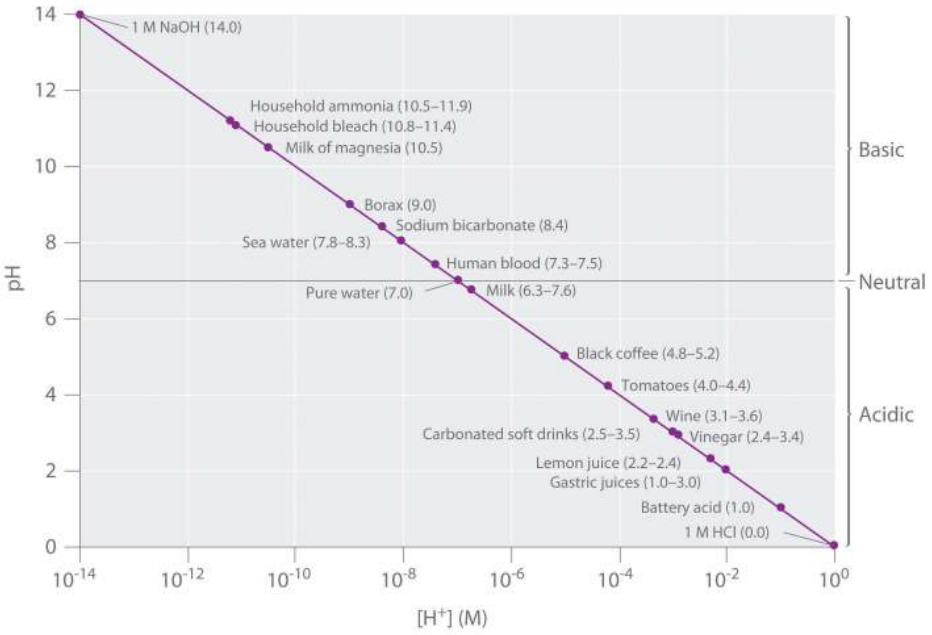


Figure 9.5.2: A Plot of pH versus $[H^+]$ for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 9.5.2

Label each solution as acidic, basic, or neutral based only on the stated ***pH***.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Solution

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

Exercise 9.5.2

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. slightly basic

b. basic

c. acidic

Measuring pH

Tools have been developed that make the measurement of pH simple and convenient. For example, pH paper (Figure 9.5.3)consists of strips of paper impregnated with one or more **acid-base indicators**, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its

color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration (Figure **9.5.3**).



Figure **9.5.3**: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. (right) These three meters and probes can measure pH (left) and electrical conductivity (center and right). Photos by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{9.5.1}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{9.5.2}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{9.5.3}$$

$$\mathrm{H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)} \tag{9.5.4}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the

destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure **9.5.4**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

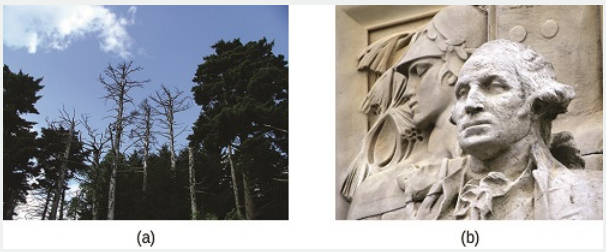


Figure **9.5.4**: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

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9.6: Working with pH

Learning Objectives

- Calculate pH from $[H_3O^+]$ and $[H_3O^+]$ from pH.

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".

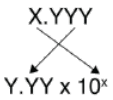
If you get a different answer, or an error, try pressing the LOG key before you enter the number.

Example 9.6.2: 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

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. $[H_3O^+] = 1 \times 10^{-3}$ M b. $[H_3O^+] = 2.5 \times 10^{-11}$ M c. $[H_3O^+] = 4.7 \times 10^{-9}$ M Find: ? pH
Plan the problem.	Need to use the expression for pH (Equation ???). $pH = - \log [H_3O^+]$
Calculate.	Now substitute the known quantity into the equation and solve. a. $pH = - \log [1 \times 10^{-3}] = 3.0$ (1 decimal places since 1 has 1 significant figure) b. $pH = - \log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures) c. $pH = - \log [4.7 \times 10^{-9}] = 8.30$ (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 9.6.2

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 ??? for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[H_3O^+] = \text{antilog}(-pH) \tag{9.6.1}$$

or

$$[H_3O^+] = 10^{-pH} \tag{9.6.2}$$

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 9.6.3: 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

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 9.6.2). $[H_3O^+]$ = 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 $[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ 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: X.YYY → Y.YY x 10^x

Exercise 9.6.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5 x 10^{-8} M

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9.7: Acid-base equilibrium

Most of the acid-base reactions are equilibrium reactions, i.e., the reactants form the products, and the products react to re-form the reactants. The reaction is shown with double arrows to indicate that both the forward and the reverse reactions happen simultaneously.

Pre-equilibrium and equilibrium

Initially, there are only reactants present. The concentration of the reactants decreases over time as they convert to the products. The rate of the reaction is proportional to the concentration of the reactants. So, the rate of the forward reaction decreases over time. The products build up over time. The products react with each other to re-form the reactants, i.e., the reverse reaction. The rate of the reverse reaction increases over time as the concentration of the products increases, until the rate of reverse reaction becomes equal to the rate of the forward reaction, as illustrated in Fig. 6.4.1

- At the beginning of the equilibrium when the rate of the reverse reaction is slower than the rate of forward reaction is the pre-equilibrium phase.
- The equilibrium phaes starts at the point when the rate of reverse reaction becomes equal to the rate of the forward reaction

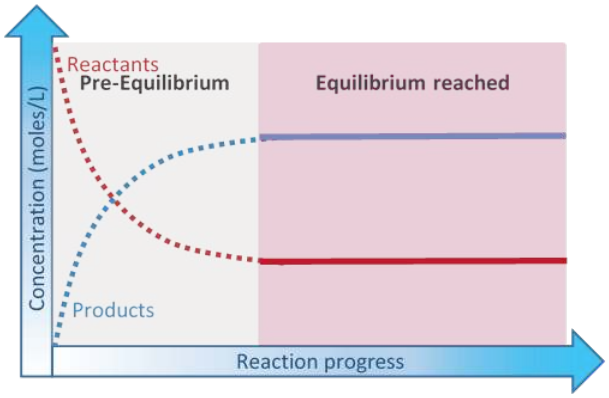


Figure **9.7.1**: In pre-equilibrium, reactants react and their concentration, and, consequently, the rate of forward reaction decreases over time. The products build-up and the reverse reaction increases over time. When rate of forward reaction becomes equal to the rate of reverse reaction the equilibrium is reached and the concentration of reactants and products do not change.

At the point when the rate of reverse reaction becomes equal to the rate of the forward reaction, **equilibrium** has reached. The concentration of the reactants and products do not change at equilibrium because they are consumed and re-formed at the same rate –it is a dynamic equilibrium.

The equilibrium reactions are not limited to acid-base reactions; they are common in all types of chemical reactions. Fig. 6.4.2 illustrates the concentrations and rates of reactions changes in pre-equilibrium and equilibrium phases with the help of an actual chemical equilibrium reaction between a decomposition reaction of a colorless gas N_2O_4 and its reverse reaction, i.e., a combination reaction of brown color gas NO_2.

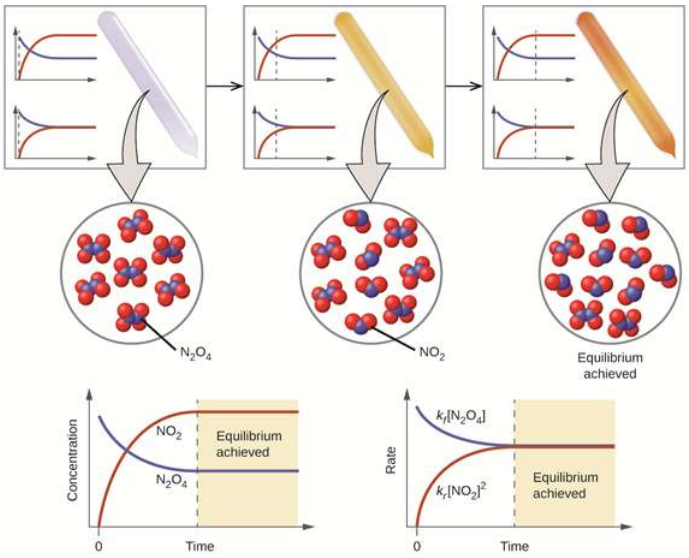


Figure **9.7.2**: Top row: a sealed tube containing colorless gas N_2O_4 darkens as it decomposes to yield brown gas NO_2 by the reaction: $\mathbf{N_2O_4 \rightleftarrows 2NO_2}$. The middle row: shows the models of the molecules at the timeline marked by the dotted lines in the graphs. Bottom row: shows concentration vs time (left graph); rate of forward reaction by blue curve and rate of reverse reaction by red curve (right graph). Source: OpenStax / CC BY (https://creativecommons.org/licenses/by/4.0)

What happens when a chemical equilibrium is disturbed?

The concentration of the reactants and products does not change in the mixture when the reaction is at equilibrium because the rate of the forward reaction is equal to the rate of the reverse reaction. Any change made at the equilibrium adds stress to the equilibrium. The system moves in a way to relieve the stress. For example, if one of the reactants is added to the mixture, the rate of forward reaction increases removing the added reactant until a new equilibrium establishes, i.e., the system relieves the stress by removing the added reactant.

Le Chatelier's principle

If a chemical equilibrium is disturbed, the rates of forward and reverse reactions change to relieve the stress and re-establish the equilibrium.

The stresses can be changes in the concentration, pressure, or temperature, as explained in the following section.

Effect of concentration on a chemical equilibrium

The following are the consequences of concentration changes on a chemical reaction at equilibrium.

1. If a reactant is added, the forward reaction increases to remove the reactant.
2. If a reactant is removed, the forward reaction decreases; consequently, the reverse reaction adds the reactant.
3. If a product is added, the reverse reaction increases to remove the product.
4. If a product is removed, the reverse reaction decreases; consequently, the forward reaction adds the product.

Fig. 6.4.3 illustrates the effects with the help of water level in two tanks connected through a conduit in the left tank representing reactants and in the right tank representing products.

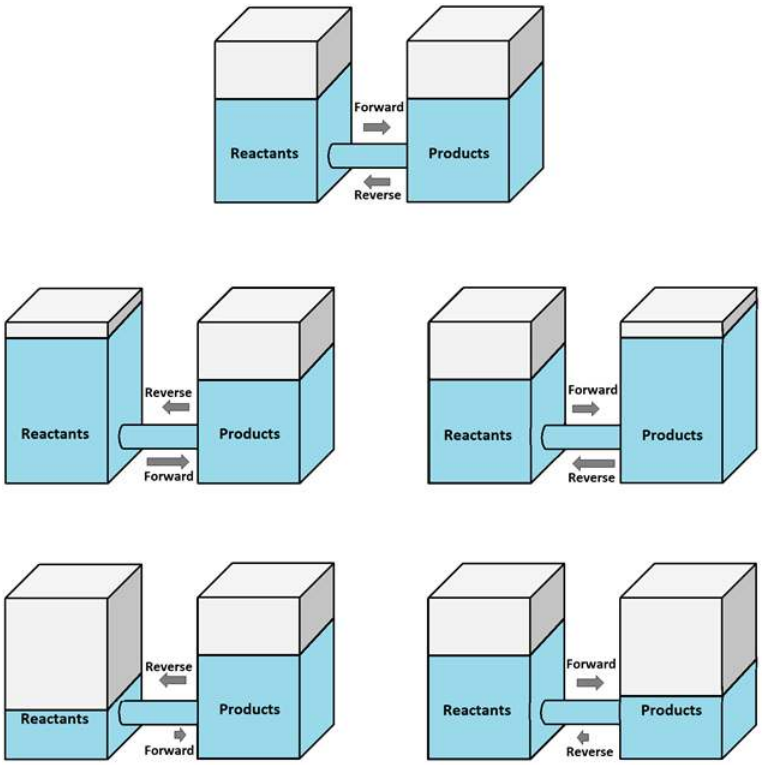


Figure **9.7.3**: Illustration of Le Chatelier's principle using two water tanks connected through a conduit; 1) at equilibrium the rate of forward and reverse reactions are equal (the topmost), 2) when any reactant is increased the forward reaction rate increase (middle left), 3) when any product is increased the reverse reaction rate increases (middle right), 4) when any reactant is decreased the forward reaction rate decreases (bottom left), and 5) when any product is decreased the reverse reaction decreases (bottom right)

Fig 6.4.4 demonstrates the effect of concentration change on the chemical equilibrium between brown dichromate ions and yellow chromate ions:



Figure **9.7.4**: Demonstration of effect of concentration change on chemical equilibrium: $\mathbf{Cr_2O_7^{2-}(aq,\ brown\ ) + H_2O(I) \rightleftarrows 2CrO_4^{2-}(aq,\ yellow\ ) + 2H^+(aq)}$. Addition of H^+ to the tube on left by adding HNO_3 shifts the equilibrium to left making more of brown $Cr_2O_7^{2-}$ shown in the middle tube. Removal of H^+ by adding a base NaOH shift the reaction to the right making more of yellow CrO_4^{2-} shown in right most tube. Source: NCSSMDistanceEd / CC BY (https://creativecommons.org/licenses/by/3.0)

$$\mathbf{Cr_2O_7^{2-}(aq,\ brown\ ) + H_2O(I) \rightleftarrows 2CrO_4^{2-}(aq,\ yellow\ ) + 2H^+(aq)}$$

The addition of acid to the test tube on the left increases H^+ in the system, increasing reverse reaction, which can be observed by the increased brown color in the middle test tube. Then, the addition of a base removes H^+ from the system by an acid-base reaction: $\mathbf{H^+ + OH^- \rightarrow H_2O}$. The decrease in H^+ shifts the equilibrium to the product side, which can be observed by the increased yellow color in the test tube on the right.

A practical example of the effect of concentration on a chemical equilibrium is the binding of oxygen (O_2) with hemoglobin (Hb) during the breathing process.

$$Hb(aq) + O_2(g) \rightleftarrows HbO_2(aq)$$

The concentration of oxygen is higher in the lunges that shift the equilibrium to the product side, binding more oxygen with the hemoglobin. When the blood arrives in tissues, the concentration of oxygen is lower in tissues, causing the equilibrium to shift to the reactant side, releasing the oxygen.

The oxygen concentration decreases as the altitude increases. The mountain climbers may experience hypoxia, i.e., inadequate supply of oxygen to the body because the lower level of oxygen at high altitude may shift the equilibrium to the right, resulting in less binding of oxygen with the hemoglobin in the lungs. The body reacts by producing more hemoglobin, but it takes about 10 days for the body to re-adjust the hemoglobin level in the blood. Peoples living at higher altitudes usually have a higher level of hemoglobin in their blood for the reasons described above.

Effect of pressure on a chemical equilibrium

Changes in pressure do not affect the concentration of solids and liquid. However, an increase in pressure decreases the volume, and, consequently, increases the concentration of gases, as illustrated in Fig. 6.4.5.

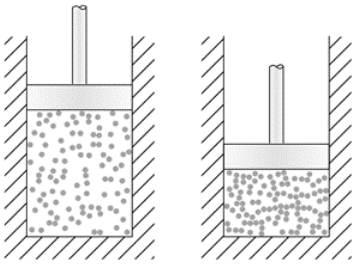


Figure **9.7.5**: Illustration of increase in pressure causes decrease in the volume and increase in the concentration of gas molecules. Source: Olivier Cleynen / CC0

> If a chemical equilibrium involves gases, an increase in pressure has the same effect as increases in the gaseous reactant or product—the equilibrium shifts in the direction where there are fewer moles of gases.

Fig. 6.4.6 demonstrated this effect for the equilibrium between colorless N_2O_4 gas and brown color NO_2 gas:

$$N_2O_4(g,\ \text{colorless}) \rightleftarrows 2NO_2(g,\ \text{brown})$$

The color becomes light in going from a syringe on the right to the syringe in the middle. It can be explained based on the fact that the concentration of gases decreased upon an increase in volume as a result of a decrease in pressure. Then the color becomes darker over time, as shown by the syringe on the right. The darker color indicates that the equilibrium has shifted to the product side where there are more moles of gas, to relieve the stress.

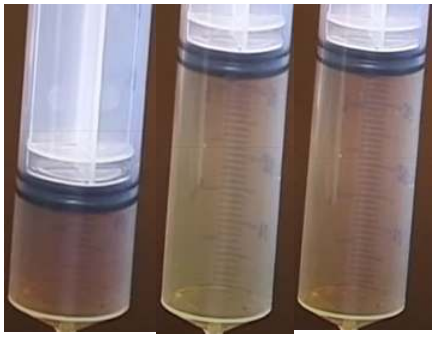


Figure **9.7.6**: Decrease in pressure on the equilibrium: $N_2O_4(g,\ \text{colorless}) \rightleftarrows 2NO_2(g,\ \text{brown})$, Middle syringe → syringe on the right, increases the forwared reaction to release the stress. Source: NCSSMDistanceEd / CC BY (https://creativecommons.org/licenses/by/3.0)

Effect of temperature on a chemical equilibrium

Exothermic reaction releases heat, i.e., heat is one of the products. If the forward reaction is exothermic, the reverse reaction must be endothermic by the same amount and vice versa.

> When a reversible reaction at equilibrium is disturbed by increasing temperature, the equilibrium shifts in the endothermic direction of the reaction to remove the heat and vice versa.

In the equilibrium between colorless N_2O_4 and brown color NO_2 gases, the reaction is endothermic in the forward direction:

$$\mathbf{N_2O_4}(g,\ \textbf{colorless}) + \textbf{Heat} \rightleftarrows \mathbf{2NO_2}(g,\ \textbf{brown})$$

An increase in temperature shifts the equilibrium in the endothermic direction to relieve the stress, as demonstrated in Fig. 6.4.7.



Figure **9.7.7**: Increase in temperature shifts the equilibrium in the endothermic direction producing more of the colored NO_2 in the following equilibrium: $\mathbf{N_2O_4}(g,\ \textbf{colorless}) + \textbf{Heat} \rightleftarrows \mathbf{2NO_2}(g,\ \textbf{brown})$. An overlay of the same 99.9% pure NO_2/N_2O_4 sealed in an ampoule. From left to right -196 °C, 0 °C, 23 °C, 35 °C, 50 °C. Source: Eframgoldberg / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

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9.8: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

- Define *Le Chatelier's principle*.
- Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 9.8.1

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In which direction—toward reactants or toward products-—does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Exercise 9.8.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

How does an equilibrium react to a change in pressure? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to

the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 9.8.2

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Exercise 9.8.2

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts toward reactants.

What is the effect of temperature changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

endothermic: energy + reactants → products

exothermic: reactants → products + energy

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

Example 9.8.3

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Exercise 9.8.3

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

Chemistry is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?



Figure **9.8.1** Garden Equilibria © Thinkstock. This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil, and the ability of plants to absorb it, is dependent upon the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue, as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercise 9.8.1

1. Define *Le Chatelier's principle*.
2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53kJ \rightleftharpoons 2HI(g)$$

a. decreased temperature
b. increased pressure
c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546kJ$$

a. increased temperature
b. addition of H_2
c. decreased pressure

5. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196kJ$$

a. removal of SO_3
b. addition of O_2
c. decreased temperature

6. Given this equilibrium, predict the direction of shift for each stress.

$$CO_2(g) + C(s) + 171kJ \rightleftharpoons 2CO(g)$$

a. addition of CO
b. increased pressure
c. addition of a catalyst

7. The synthesis of NH_3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$$

Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.

8. The synthesis of $CaCO_3$ uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180kJ$$

Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
2.
3. a. toward reactants

- toward reactants
- toward products
-
- a. toward products
  b. toward products
  c. toward products
-
- increased pressure, decreased temperature, removal of NH_3

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9.9: 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**:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

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:

$$\mathrm{H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)}$$

After removing the spectator ions, we get the net ionic equation:

$$\mathrm{H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l)}$$

When a strong acid and a strong base are combined in the proper amounts—when $[\mathrm{H^+}]$ equals $[\mathrm{OH^-}]$\)—a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. 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 9.9.1: 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 ($\mathrm{CH_3CH_2CO_2H}$) with aqueous calcium hydroxide [$\mathrm{Ca(OH)_2}$].

Solution

Solutions to Example 14.5.1

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 9.9.1

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

Answer

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

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.

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

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.

$$\mathbf{Zn\,(s) + 2\,NaOH\,(aq) + 2\,H_2O\,(l) \longrightarrow Na_2Zn(OH)_4\,(aq) + H_2\,(g).}$$

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9.10: Acids and Bases in Industry and in Daily Life

Learning Objective

- Know the many uses of common acids and bases.

Antacids: A Basic Remedy

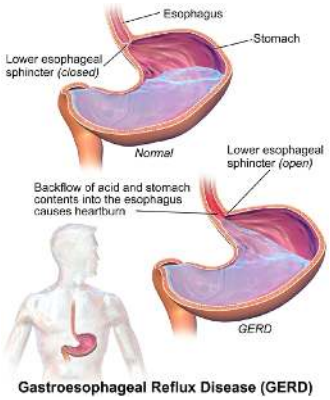


Figure **9.10.1**. Antacids are available over the counter and are taken by mouth to quickly relieve occasional heartburn, the major symptom of gastroesophageal reflux disease and also indigestion. Treatment with antacids alone is symptomatic and only justified for minor symptoms.

Antacids contain alkaline ions that chemically neutralize stomach gastric acid, reducing damage and relieving pain. For example, Tums is a very commonly used antacid that can be bought over the counter. Other antacids, such as Alka Seltzer, work in similar ways. Below, show the mechanism and products for reaction in which calcium carbonate (the active ingredient in Tums) neutralizes HCl in a simple proton transfer reaction.

$$CaCO_3\,(s) + HCl\,(aq) \rightarrow H_2CO_3\,(aq) + CaCl_2\,(aq)$$

Following this acid-base reaction, carbonic acid quickly degrades into CO_2 and H_2O.

$$H_2CO_3\,(aq) \rightarrow CO_2(g) + H_2O(l)$$

***Figure* 9.10.1** *A comparison of a healthy condition to GERD. I*

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Under the generic name algeldrate, aluminium hydroxide is used as an antacid. Aluminium hydroxide is preferred over other alternatives such as sodium bicarbonate because $Al(OH)_3$, being insoluble, does not increase the pH of stomach above 7 and hence, does not trigger secretion of excess stomach acid. Brand names include Alu-Cap, Aludrox, Gaviscon, and Pepsamar. In 2016 Gaviscon was one of the biggest selling branded over-the-counter medications sold in Great Britain, with sales of £62 million. It reacts with excess acid in the stomach, reducing the acidity of the stomach content, which may relieve the symptoms of ulcers, heartburn or dyspepsia. Such products can cause constipation, because the aluminum ions inhibit the contractions of smooth muscle cells in the gastrointestinal tract, slowing peristalsis and lengthening the time needed for stool to pass through the colon. Some such products are formulated to minimize such effects through the inclusion of equal concentrations of magnesium hydroxide or magnesium carbonate, which have counterbalancing laxative effects.

Antacids are distinct from acid-reducing drugs like H_2-receptor antagonists or proton pump inhibitors and they do not kill the bacteria *Helicobacter pylori*, which causes most ulcers. Ranitidine (Zantac), famotidine (Pepcid AC), and cimetidine (Tagamet) are in a class of medications called H_2 blockers. It decreases the amount of acid made in the stomach and are used to treat ulcers; gastroesophageal reflux disease (GERD), a condition in which backward flow of acid from the stomach causes heartburn and injury of the food pipe (esophagus); and conditions where the stomach produces too much acid, such as Zollinger-Ellison syndrome. These over-the-counter medications are used to prevent and treat symptoms of heartburn associated with acid indigestion and sour

stomach. Omeprazole (Prilosec) also works by decreasing the amount of acid made in the stomach and is in a class of medications called proton-pump inhibitors.

Acids and Bases in Industry and at Home

Common Acids

It should not be hard for you to name several common acids, but you might find that listing bases is just a little more difficult. Here's a partial list of some common acids, along with some chemical formulas:

Table **9.10.1** Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the "fiz" in carbonated drinks	As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. One of the most important applications of hydrochloric acid is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing. Another major use of hydrochloric acid is in the production of organic compounds, such as vinyl chloride and dichloroethane for PVC. Other organic compounds produced with hydrochloric acid include bisphenol A for polycarbonate, activated carbon, and ascorbic acid, as well as numerous pharmaceutical products. Other inorganic compounds produced with hydrochloric acid include road application salt calcium chloride, nickel(II) chloride for electroplating, and zinc chloride for the galvanizing industry and battery production.

Sulfuric Acid

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. World production in the year 2004 was about 180 million tonnes, with the following geographic distribution: Asia 35%, North America (including Mexico) 24%, Africa 11%, Western Europe 10%, Eastern Europe and Russia 10%, Australia and Oceania 7%, South America 7%. Most of this amount (≈60%) is consumed for fertilizers, particularly superphosphates, ammonium phosphate and ammonium sulfates. About 20% is used in chemical industry for production of detergents, synthetic resins, dyestuffs, pharmaceuticals, petroleum catalysts, insecticides and antifreeze, as well as in various processes such as oil well acidicizing, aluminium reduction, paper sizing, water treatment. About 6% of uses are related to pigments and include paints, enamels, printing inks, coated fabrics and paper, and the rest is dispersed into a multitude of applications such as production of explosives, cellophane, acetate and viscose textiles, lubricants, non-ferrous metals, and batteries.



Figure **9.10.2**: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

Because the hydration of sulfuric acid is thermodynamically favorable (and is highly exothermic) and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating property, removing water ($\mathbf{H_2O}$) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation ???).

Nitric Acid

Nitric acid ($\mathbf{HNO_3}$) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. The main industrial use of nitric acid is for the production of fertilizers. Nitric acid is neutralized with ammonia to give ammonium nitrate. This application consumes 75–80% of the 26 million tonnes produced annually (1987). The other main applications are for the production of explosives, nylon precursors, and specialty organic compounds.



Figure **9.10.3**: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Table **9.10.2** *Common Bases and Its Uses*

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula **NaOH**.

It is a popular strong base used in industry. Around 56% of sodium hydroxide produced is used by industry, 25% of which is used in the paper industry. Sodium hydroxide is also used in the manufacture of sodium salts and detergents, pH regulation, and organic synthesis. It is used in the Bayer process of aluminium production. In bulk, it is most often handled as an aqueous solution, since solutions are cheaper and easier to handle.

Sodium hydroxide is used in many scenarios where it is desirable to increase the alkalinity of a mixture, or to neutralize acids.



Figure **9.10.4** Sample of sodium hydroxide as pellets in a watchglass. (Public Domain; Walkerma).

Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathbf{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime.

One significant application of calcium hydroxide is as a flocculant, in water and sewage treatment. It is also used in fresh water treatment for raising the pH of the water so that pipes will not corrode where the base water is acidic, because it is self-regulating and does not raise the pH too much.

It is also used in the preparation of ammonia gas (NH_3), using the following reaction:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

Another large application is in the paper industry, where it is an intermediate in the reaction in the production of sodium hydroxide. Because of its low toxicity and the mildness of its basic properties, slaked lime is widely used in the food industry:

Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula $\mathbf{NH_3}$ and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

Globally, approximately 88% (as of 2014) of ammonia is used as fertilizers either as its salts, solutions or anhydrously. When applied to soil, it helps provide increased yields of crops such as maize and wheat. 30% of agricultural nitrogen applied in the US is in the form of anhydrous ammonia and worldwide 110 million tonnes are applied each year. Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

Common acids and bases have many and various uses in industry and in daily life.

Contributors and Attributions

-
- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
- Wikipedia
- TextMap: Chemistry-A Molecular Approach (Tro)

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- Henry Agnew (UC Davis)
- MedlinePlus

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9.11: 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 $\mathbf{OH^-(aq)}$ ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$\mathbf{HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-(aq)} \tag{9.11.1}$$

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:

$$\mathbf{H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq)} \tag{9.11.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure **9.11.1** illustrates both actions of a buffer.

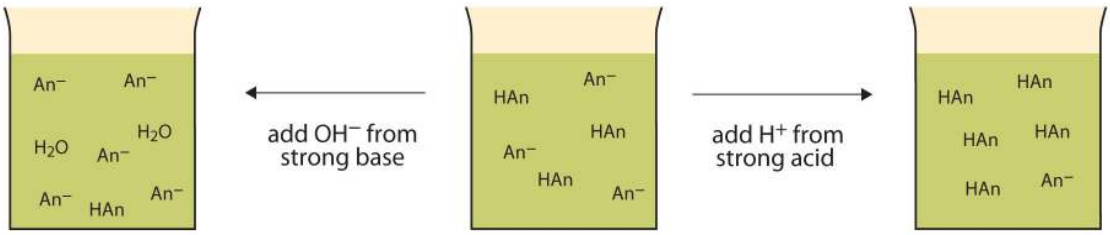


Figure **9.11.1**: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

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:

$$\mathbf{NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)} \tag{9.11.3}$$

while the **ammonium ion** ($\mathbf{NH_4^+(aq)}$) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell) \quad (9.11.4)$$

Example 9.11.1: 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 9.11.1

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.

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CHAPTER OVERVIEW

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10.1: Prelude to Organic Chemistry - Alkanes and Halogenated Hydrocarbons

Hydrocarbons are the simplest organic compounds, but they have interesting physiological effects. These effects depend on the size of the hydrocarbon molecules and where on or in the body they are applied. Alkanes of low molar mass—those with from 1 to approximately 10 or so carbon atoms—are gases or light liquids that act as anesthetics. Inhaling ("sniffing") these hydrocarbons in gasoline or aerosol propellants for their intoxicating effect is a major health problem that can lead to liver, kidney, or brain damage or to immediate death by asphyxiation by excluding oxygen.

Swallowed, liquid alkanes do little harm while in the stomach. In the lungs, however, they cause "chemical" pneumonia by dissolving fatlike molecules from cell membranes in the tiny air sacs (alveoli). The lungs become unable to expel fluids, just as in pneumonia caused by bacteria or viruses. People who swallow gasoline or other liquid alkane mixtures should not be made to vomit, as this would increase the chance of getting alkanes into the lungs. (There is no home-treatment antidote for gasoline poisoning; call a poison control center.)



Figure **10.1.1**: Butane is a hydrocarbon with the formula $\mathbf{C_4H_{10}}$ and is a gas at room temperature and atmospheric pressure. Under excess pressures, it can be liquidized like the fuel shown in this butane lighters. (CC BY 3.0Unported; Frank Vincentz)

Liquid alkanes with approximately 5–16 carbon atoms per molecule wash away natural skin oils and cause drying and chapping of the skin, while heavier liquid alkanes (those with approximately 17 or more carbon atoms per molecule) act as emollients (skin softeners). Such alkane mixtures as mineral oil and petroleum jelly can be applied as a protective film. Water and aqueous solutions such as urine will not dissolve such a film, which explains why petroleum jelly protects a baby's tender skin from diaper rash.

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10.2: Organic Chemistry

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride ($\mathrm{NH_4Cl}$), expecting to get ammonium cyanate ($\mathrm{NH_4OCN}$). What he expected is described by the following equation.

$$\mathrm{AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN} \tag{10.2.1}$$

Instead, he found the product to be urea ($\mathrm{NH_2CONH_2}$), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **10.2.1**.

Table **10.2.1**: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane		Inorganic	NaCl
low melting points	−95°C		high melting points	801°C
low boiling points	69°C		high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable		nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds		exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **10.2.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **10.2.1**.

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10.3: Structures and Names of Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure **10.3.1**.

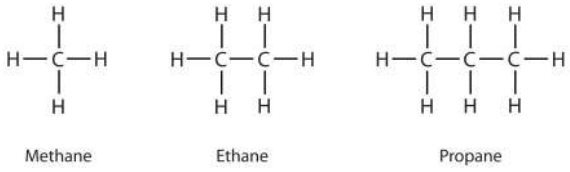


Figure **10.3.1**: The Three Simplest Alkanes

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 **10.3.2**).

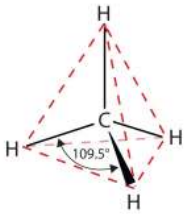


Figure **10.3.2**: The Tetrahedral Methane Molecule

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 **10.3.1**.

Table **10.3.1**: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure **10.3.3**. 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.

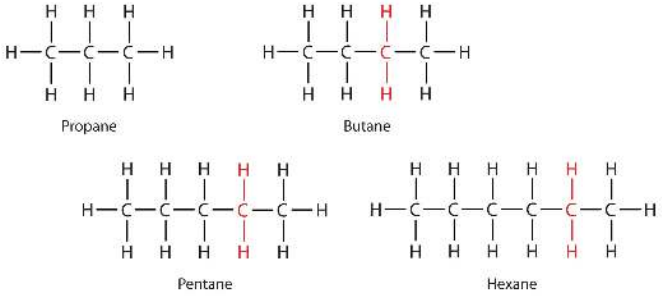


Figure **10.3.3**: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

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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10.4: Branched-Chain Alkanes

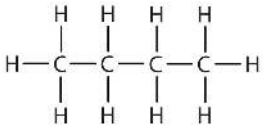
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

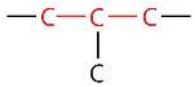
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

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



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



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

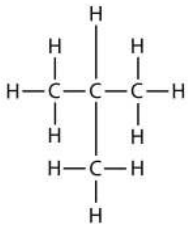


Figure 10.4.1).

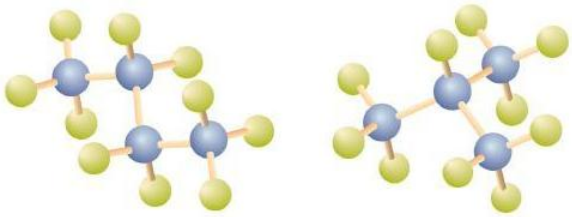
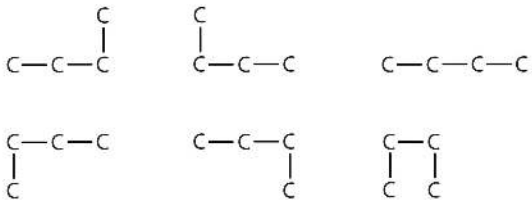


Figure 10.4.1: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

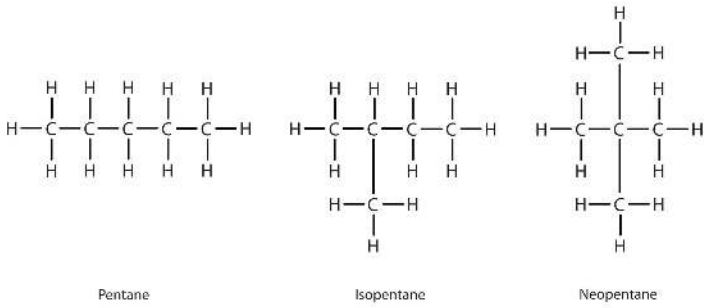
Notice that C_4H_{10} is depicted with a bent chain in Figure 10.4.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **10.4.1**.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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10.5: Condensed Structural and Line-Angle Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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10.6: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

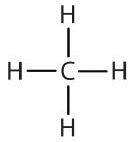
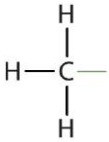
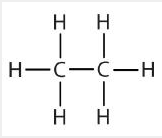
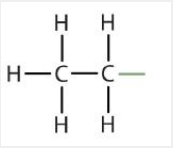
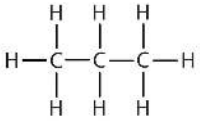
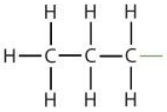
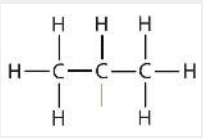
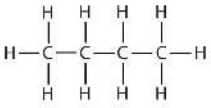
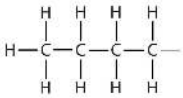
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table **10.6.1**) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table **10.6.1**: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $-CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table **10.6.2**. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table **10.6.2**: Common Alkyl Groups

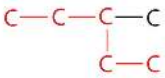
Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		$CH_3–$
ethane		ethyl		$CH_3CH_2–$
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl*		$CH_3CH_2CH_2CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example **10.6.1**).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.

2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

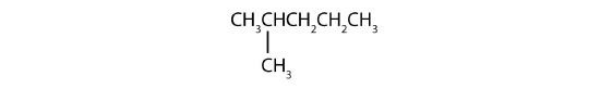


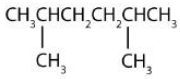
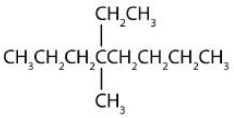
3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 10.6.1

Name each compound.

1. 

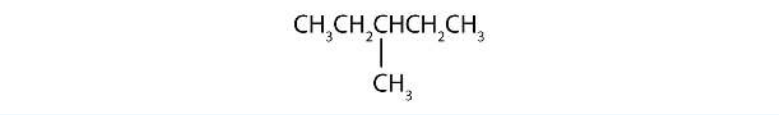
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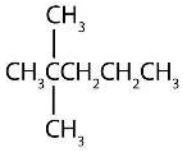
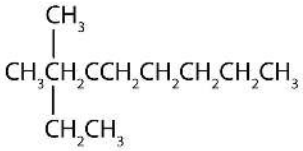
Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

Exercise 10.6.1

Name each compound.

1. 

- 
- 

Example 10.6.2

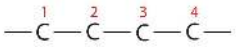
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

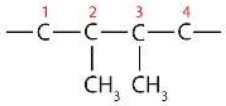
Solution

In drawing structures, always start with the parent chain.

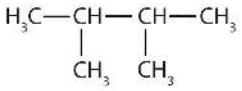
a. The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.

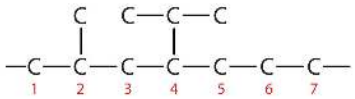


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.

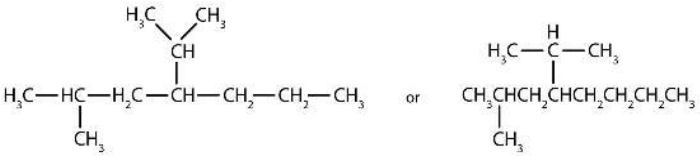


- The parent chain is heptane in this case, indicating seven carbon atoms in the LCC. –C–C–C–C–C–C–C–

  Adding the groups at their proper positions gives



  Filling in all the hydrogen atoms gives the following condensed structural formulas:



  Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

? Exercise 10.6.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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10.7: Physical Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table **10.7.1** describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table **10.7.1**: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure **10.7.1**: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table **10.7.1** indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table **10.7.1** are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

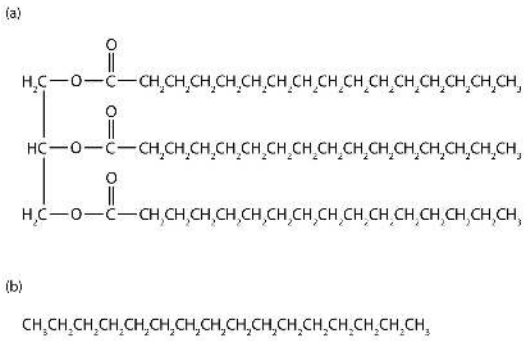


Figure **10.7.2**: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

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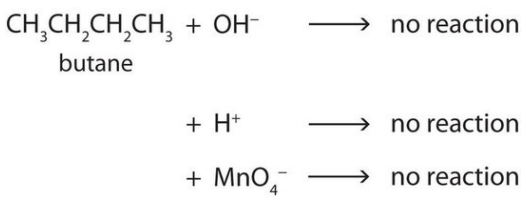
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10.8: Chemical Properties of Alkanes

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:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{10.8.1}$$

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:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{10.8.2}$$

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).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{10.8.3}$$

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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10.9: Halogenated Hydrocarbons

Learning Objectives

- To name halogenated hydrocarbons given formulas and write formulas for these compounds given names.

Many organic compounds are closely related to the alkanes. As we noted previously, alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce halogenated hydrocarbons, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:



The replacement of only one hydrogen atom gives an alkyl halide (or haloalkane). The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*. The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location. The prefixes are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. Thus CH_3CH_2Cl has the common name ethyl chloride and the IUPAC name chloroethane. Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 10.9.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2$–) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

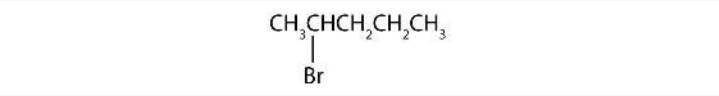
Exercise 10.9.1

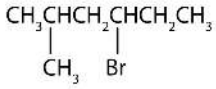
Give common and IUPAC names for each compound.

a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

Example 10.9.2

Give the IUPAC name for each compound.

1. 

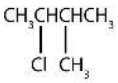


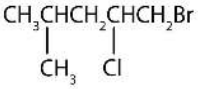
Solution

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl (CH_3) and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

? Exercise 10.9.2

Give the IUPAC name for each compound.

a. 



A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table **10.9.1**, along with some of their uses.

Table **10.9.1**: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

To Your Health: Chlorofluorocarbons and the Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table 10.9.1.

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is

hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

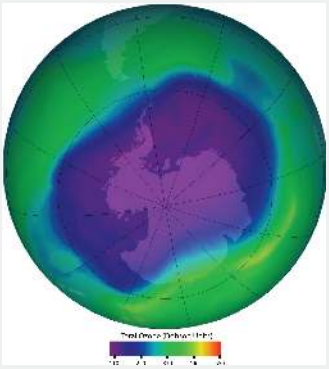


Figure **10.9.1**: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, Ozone watch (opens in new window) [ozonewatch.gsfc.nasa.gov].

Key Takeaway

- The replacement of an hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound.

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10.10: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6. Each carbon atom has two hydrogen atoms attached (Figure **10.10.1**) and is called cyclopropane.

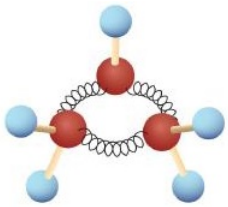
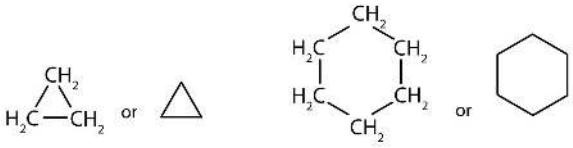


Figure **10.10.1**: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example **10.10.1** interprets the name of a cycloalkane with a single substituent group.

Example 10.10.1

Draw the structure for each compound.

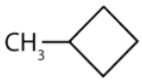
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



- The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



? Exercise 10.10.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

> The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure **10.10.1**.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

Key Takeaway

- Many organic compounds have cyclic structures.

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10.11: Prelude to Unsaturated and Aromatic Hydrocarbons

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene).

The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($CHBrClCF_3$).

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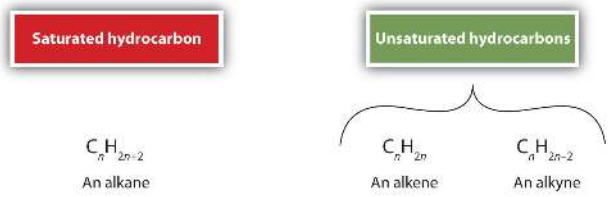
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10.12: Alkenes- Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

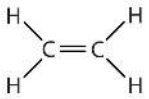


Some representative alkenes—their names, structures, and physical properties—are given in Table **10.12.1**.

Table **10.12.1**: 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 **10.12.1**. 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 **10.12.1**, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure **10.12.1**). 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.

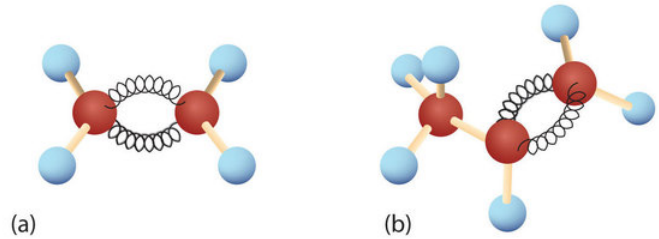
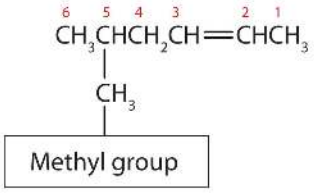


Figure **10.12.1**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

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.

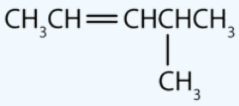
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

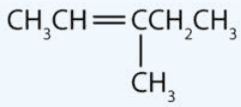
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or 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 10.12.1

Name each compound.

a. 

b. 

Solution

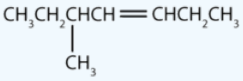
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 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 10.12.1

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 10.12.2

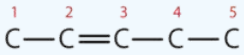
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

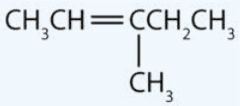
Solution

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:

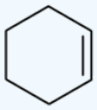


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



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 10.12.2

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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10.13: Cis-Trans Isomers (Geometric Isomers)

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure **10.13.1**.

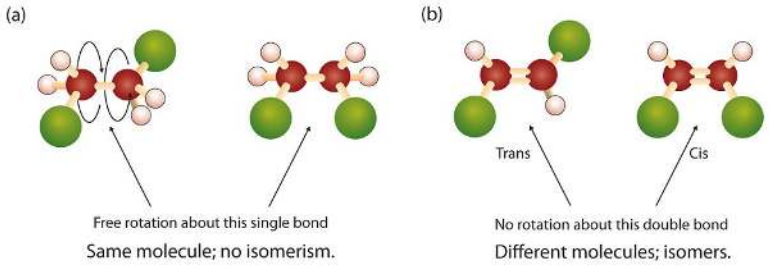


Figure **10.13.1**: *Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure **10.13.1**), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (Figure **10.13.1***b*), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure **10.13.2**).

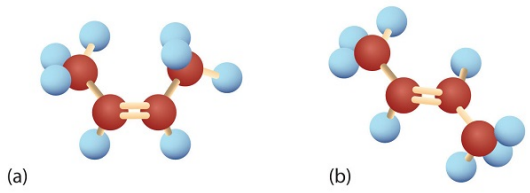


Figure **10.13.2**: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:



Figure* 10.13.3: Models of (left) Cis-2-Butene and (right) Trans-2-Butene.*

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure **10.13.4**). We can draw two *seemingly* different propenes:



Figure* 10.13.4: Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Advanced Note: E/Z Isomerization

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E,Z Convention [E] [E] [E] discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



Example 10.13.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. $CHCl=CHBr$
2. $CH_2=CBrCH_3$
3. $(CH_3)_2C=CHCH_2CH_3$
4. $CH_3CH=CHCH_2CH_3$

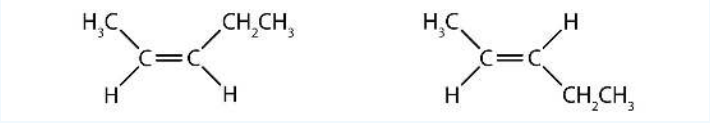
Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:

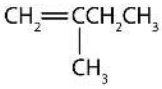


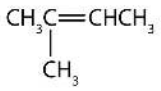
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



Exercise 10.13.1

Which compounds can exist as cis-trans isomers? Draw them.

a. $CH_2=CHCH_2CH_2CH_3$
b. $CH_3CH=CHCH_2CH_3$
c. $CH_3CH_2CH=CHCH_2CH_3$
d. 

e. 

Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

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10.14: Physical Properties of Alkenes

Learning Objectives

- To identify the physical properties of alkenes and describe trends in these properties.

The physical properties of alkenes are similar to those of the alkanes. The table at the start of the chapter shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.



The bright red color of tomatoes is due to lycopene—a polyene.

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene (CH_2=CHCH=CH_2) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

Key Takeaway

- The physical properties of alkenes are much like those of the alkanes: their boiling points increase with increasing molar mass, and they are insoluble in water.

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10.15: Chemical Properties of Alkenes

Learning Objectives

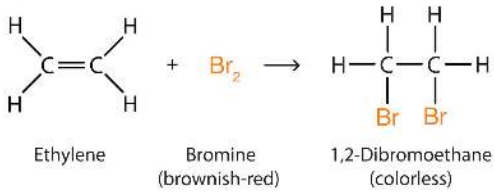
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen (H_2) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).

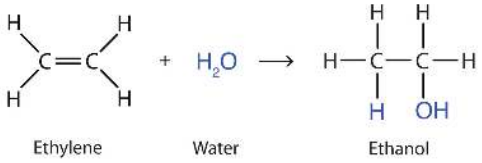


The product is an alkane having the same carbon skeleton as the alkene.

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine (Br_2) can be used to test for alkenes. Bromine solutions are brownish red. When we add a Br_2 solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:



Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):



The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

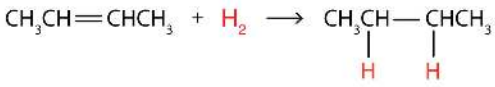
Example 10.15.1

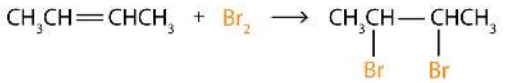
Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

a. H_2 (Ni catalyst)
b. Br_2
c. H_2O (H_2SO_4 catalyst)

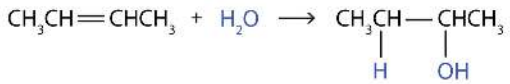
Solution

In each reaction, the reagent adds across the double bond.

a. 

b. 

or $CH_3CHBrCHBrCH_3$

c. 

or $CH_3CH_2CHOHCH_3$

? Exercise 10.15.1

Write the equation for each reaction.

a. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)
b. $CH_3CH{=}CH_2$ with Cl_2
c. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

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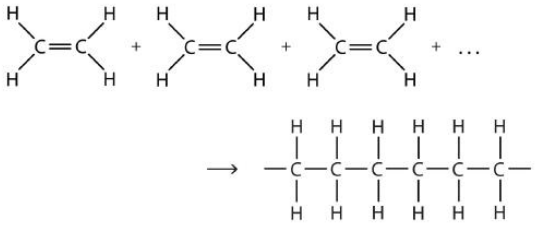
10.16: Polymers

Learning Objectives

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning “one,” and *meros*, meaning “parts”), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning “many,” and *meros*, meaning “parts”). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



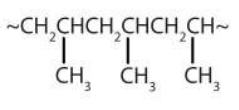
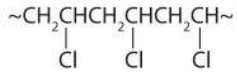
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \text{-}\mathrm{CH_2CH_2}\text{-}_n$$

Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table **10.16.1**. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table **10.16.1***: Some Addition Polymers*

Monomer	Polymer	Polymer Name	Some Uses
$CH_2=CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2=CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2=CHCl$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2=CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

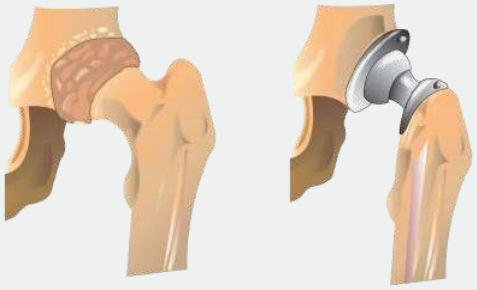


Figure **10.16.1**: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

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10.17: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure **10.17.1**). Its structure is H–C≡C–H.

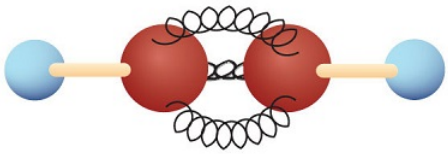


Figure **10.17.1**: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

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10.18: Aromatic Compounds- Benzene

Learning Objectives

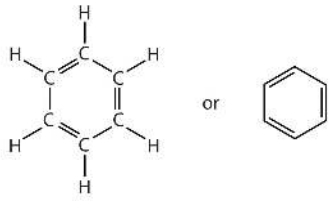
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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10.19: Structure and Nomenclature of Aromatic Compounds

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

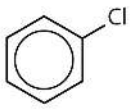
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table **10.19.1**, where the benzene ring is represented as C_6H_5.

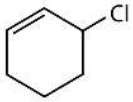
Table **10.19.1**: Some Representative Aromatic Compounds

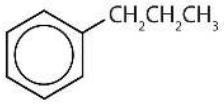
Name	Structure	Typical Uses
aniline	$C_6H_5–NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	$C_6H_5–COOH$	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	$C_6H_5–Br$	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5–NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	$C_6H_5–OH$	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5–CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

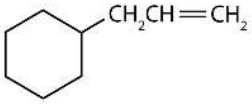
Example 10.19.1

Which compounds are aromatic?

1. 

2. 

3. 

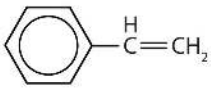
4. 

Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

? Exercise 10.19.1

Which compounds are aromatic?

1. 

2. 

3. 

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 10.19.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

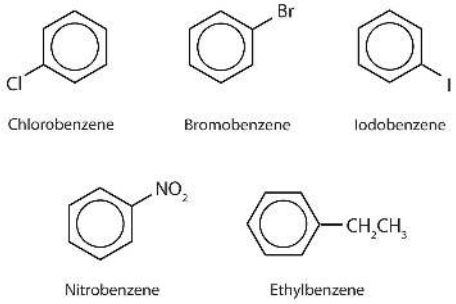


Figure 10.19.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 10.19.1.



When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure **10.19.2**). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

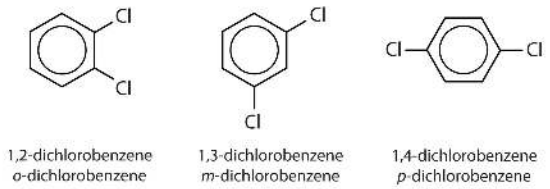
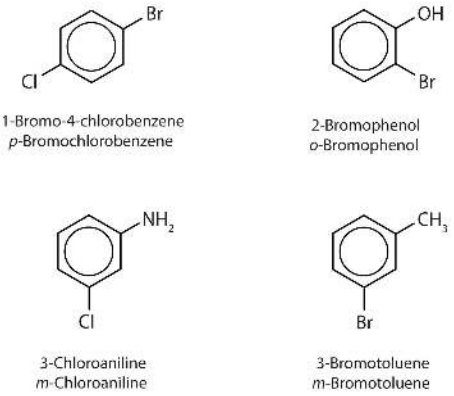


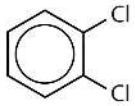
Figure **10.19.2**: The Three Isomeric Dichlorobenzenes

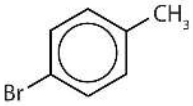
In Figure **10.19.2**, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:

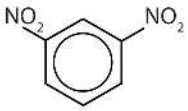


Example 10.19.2

Name each compound using both the common name and the IUPAC name.

1. 

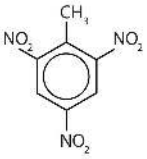
2. 

3. 

Solution

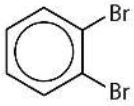
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

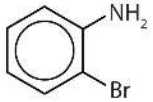
4. Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

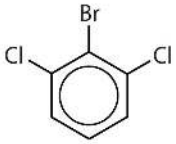


? Exercise 10.19.2

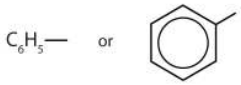
Name each compound using both the common name and the IUPAC name.

1. 

2. 

3. 

- Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



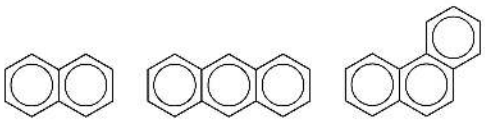
Phenyl group



2-Phenylheptane

Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



Naphthalene Anthracene Phenanthrene

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs

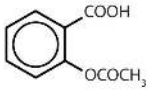
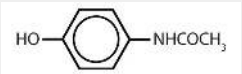
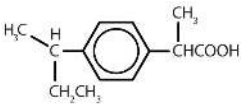
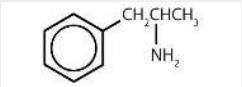
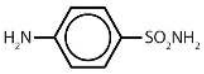
are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B_2 (riboflavin), and B_9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table **10.19.2**, also feature a benzene ring.

> So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table **10.19.2**: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

Key Takeaway

- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

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10.E: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Exercises)

12.1: Organic Chemistry

Concept Review Exercises

1. Classify each compound as organic or inorganic.
    a. C_3H_8O
    b. $CaCl_2$
    c. $Cr(NH_3)_3Cl_3$
    d. $C_{30}H_{48}O_3N$
2. Which compound is likely organic and which is likely inorganic?
    a. a flammable compound that boils at 80°C and is insoluble in water
    b. a compound that does not burn, melts at 630°C, and is soluble in water

Answers

1.
    a. organic
    b. inorganic
    c. inorganic
    d. organic
2.
    a. organic
    b. inorganic

1. Classify each compound as organic or inorganic.
    a. C_6H_{10}
    b. $CoCl_2$
    c. $C_{12}H_{22}O_{11}$
2. Classify each compound as organic or inorganic.
    a. CH_3NH_2
    b. $NaNH_2$
    c. $Cu(NH_3)_6Cl_2$
3. Which member of each pair has a higher melting point?
    a. CH_3OH and NaOH
    b. CH_3Cl and KCl
4. Which member of each pair has a higher melting point?
    a. C_2H_6 and $CoCl_2$
    b. CH_4 and LiH

Answers

1.
    a. organic
    b. inorganic
    c. organic

2.

3. a. NaOH
   b. KCl

12.2: Structures and Names of Alkanes

Concept Review Exercises

1. In the homologous series of alkanes, what is the molecular formula for the member just above C_8H_{18}?
2. Use the general formula for alkanes to write the molecular formula of the alkane with 12 carbon atoms.

Answers

1. C_9H_{20}
2. $C_{12}H_{26}$

Exercises

1. What compounds contain fewer carbon atoms than C_3H_8 and are its homologs?
2. What compounds contain five to eight carbon atoms and are homologs of C_4H_{10}?

Answer

1. CH_4 and C_2H_6

12.3: Branched-Chain Alkanes

Concept Review Exercises

1. In alkanes, can there be a two-carbon branch off the second carbon atom of a four-carbon chain? Explain.
2. A student is asked to write structural formulas for two different hydrocarbons having the molecular formula C_5H_{12}. She writes one formula with all five carbon atoms in a horizontal line and the other with four carbon atoms in a line, with a CH_3 group extending down from the first attached to the third carbon atom. Do these structural formulas represent different molecular formulas? Explain why or why not.

Answers

1. No; the branch would make the longest continuous chain of five carbon atoms.
2. No; both are five-carbon continuous chains.

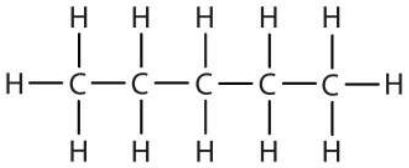
Key Takeaway

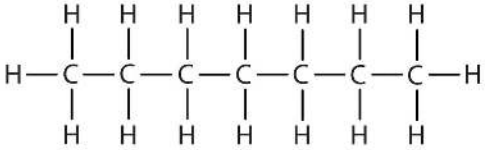
- Alkanes with four or more carbon atoms can exist in isomeric forms.

Exercises

1. Briefly identify the important distinctions between a straight-chain alkane and a branched-chain alkane.
2. How are butane and isobutane related? How do they differ?
3. Name each compound.

a.



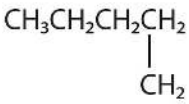
b. 

4. Write the structural formula for each compound.

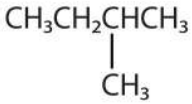
   a. hexane
   b. octane

5. Indicate whether the structures in each set represent the same compound or isomers.

   a. $CH_3CH_2CH_2CH_3$ and



   b. $CH_3CH_2CH_2CH_2CH_3$ and



Answers

1. Straight-chain alkanes and branched-chain alkanes have different properties as well as different structures.

3.

   a. pentane
   b. heptane

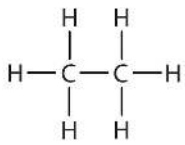
5.

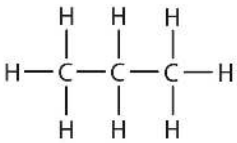
   a. no
   b. yes

12.4: Condensed Structural and Line-Angle Formulas

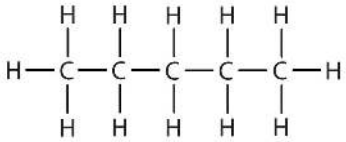
Exercises

1. Write the condensed structural formula for each structural formula.

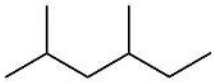
   a. 

   b. 

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c. 

2. A condensed structural formula for isohexane can be written as $(CH_3)_2CHCH_2CH_2CH_3$. Draw the line-angle formula for isohexane.
3. Draw a line-angle formula for the compound $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$.
4. Give the structural formula for the compound represented by this line-angle formula:



Answers

1.
   a. CH_3CH_3
   b. $CH_3CH_2CH_3$
   c. $CH_3CH_2CH_2CH_2CH_3$
3. 

12.5: IUPAC Nomenclature

Concept Review Exercises

1. What is a CH_3 group called when it is attached to a chain of carbon atoms—a substituent or a functional group?
2. Which type of name uses numbers to locate substituents—common names or IUPAC names?

Answers

1. substituent
2. IUPAC names

Exercises

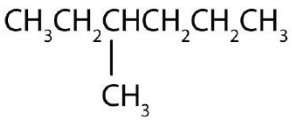
1. Briefly identify the important distinctions between an alkane and an alkyl group.
2. How many carbon atoms are present in each molecule?
   a. 2-methylbutane
   b. 3-ethylpentane
3. How many carbon atoms are present in each molecule?
   a. 2,3-dimethylbutane
   b. 3-ethyl-2-methylheptane
4. Draw the structure for each compound.
   a. 3-methylpentane
   b. 2,2,5-trimethylhexane

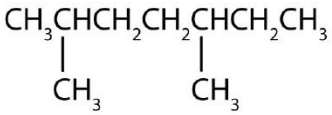
c. 4-ethyl-3-methyloctane

5. Draw the structure for each compound.

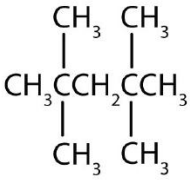
   a. 2-methylpentane
   b. 4-ethyl-2-methylhexane
   c. 2,2,3,3-tetramethylbutane

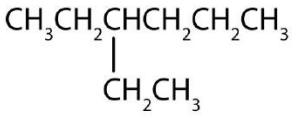
6. Name each compound according to the IUPAC system.

   a. 

   b. 

7. Name each compound according to the IUPAC system.

   a. 

   b. 

8. What is a substituent? How is the location of a substituent indicated in the IUPAC system?

9. Briefly identify the important distinctions between a common name and an IUPAC name.

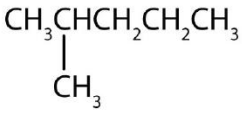
Answers

1. An alkane is a molecule; an alkyl group is not an independent molecule but rather a part of a molecule that we consider as a unit.

3.

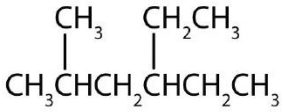
   a. 6
   b. 10

5.

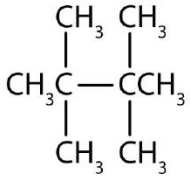
   a. 

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b.



c.



7.

a. 2,2,4,4-tetramethylpentane
b. 3-ethylhexane

9. Common names are widely used but not very systematic; IUPAC names identify a parent compound and name other groups as substituents.

12.6: Physical Properties of Alkanes

Concept Review Exercises

1. Without referring to a table, predict which has a higher boiling point—hexane or octane. Explain.
2. If 25 mL of hexane were added to 100 mL of water in a beaker, which of the following would you expect to happen? Explain.
   a. Hexane would dissolve in water.
   b. Hexane would not dissolve in water and would float on top.
   c. Hexane would not dissolve in water and would sink to the bottom of the container.

Answers

1. octane because of its greater molar mass
2. b; hexane is insoluble in water and less dense than water.

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
   a. pentane or butane
   b. heptane or nonane
2. For which member of each pair is hexane a good solvent?
   a. pentane or water
   b. sodium chloride or soybean oil

Answer

1. a. pentane
   b. nonane

12.7: Chemical Properties of Alkanes

Concept Review Exercises

1. Why are alkanes sometimes called paraffins?
2. Which halogen reacts most readily with alkanes? Which reacts least readily?

Answers

1. Alkanes do not react with many common chemicals. They are sometimes called paraffins, from the Latin parum affinis, meaning “little affinity.”
2. most readily: F_2; least readily: I_2

Exercises

1. Why do alkanes usually not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents?
2. Write an equation for the complete combustion of methane (CH_4), the main component of natural gas).
3. What is the most important reaction of alkanes?
4. Name some substances other than oxygen that react readily with alkanes.

Answers

1. Alkanes are nonpolar; they do not attract ions.

12.8: Halogenated Hydrocarbons

Concept Review Exercises

1. What is the IUPAC name for the HFC that has the formula CH_2FCF_3? (Hint: you must use a number to indicate the location of each substituent F atom.)
2. What is the IUPAC name for the HCFC that has the formula $CHCl_2CF_3$?

Answers

1. 1,1,1,2-tetrafluoroethane
2. 1,1,1-trifluoro-2,2-dichloroethane

Exercises

1. Write the condensed structural formula for each compound.
   a. methyl chloride
   b. chloroform
2. Write the condensed structural formula for each compound.
   a. ethyl bromide
   b. carbon tetrachloride
3. Write the condensed structural formulas for the two isomers that have the molecular formula C_3H_7Br. Give the common name and the IUPAC name of each.
4. Write the condensed structural formulas for the four isomers that have the molecular formula C_4H_9Br. Give the IUPAC name of each.
5. What is a CFC? How are CFCs involved in the destruction of the ozone layer?
6. Explain why each compound is less destructive to the ozone layer than are CFCs.
   a. fluorocarbons
   b. HCFCs

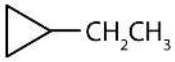
Answers

1. a. CH_3Cl
   b. $CHCl_3$
3. $CH_3CH_2CH_2Br$, propyl bromide, 1-bromopropane; $CH_3CHBrCH_3$, isopropyl bromide, 2-bromopropane
5. compounds containing Cl, F, and C; by releasing Cl atoms in the stratosphere

12.9: Cycloalkanes

Concept Review Exercises

1. What is the molecular formula of cyclooctane?
2. What is the IUPAC name for this compound?

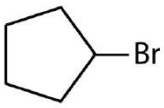


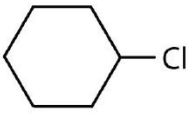
Answers

1. C_8H_{16}
2. ethylcyclopropane

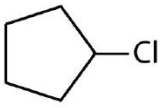
Exercises

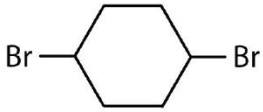
1. Draw the structure for each compound.
   a. ethylcyclobutane
   b. propylcyclopropane
2. Draw the structure for each compound.
   a. methylcyclohexane
   b. butylcyclobutane
3. Cycloalkyl groups can be derived from cycloalkanes in the same way that alkyl groups are derived from alkanes. These groups are named as cyclopropyl, cyclobutyl, and so on. Name each cycloalkyl halide.

   a. 

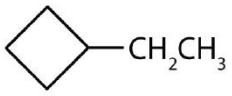
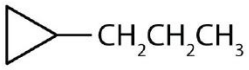
   b. 

4. Halogenated cycloalkanes can be named by the IUPAC system. As with alkyl derivatives, monosubstituted derivatives need no number to indicate the position of the halogen. To name disubstituted derivatives, the carbon atoms are numbered starting at the position of one substituent (C1) and proceeding to the second substituted atom by the shortest route. Name each compound.

   a. 

   b. 

Answers

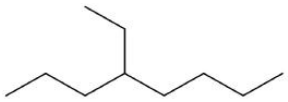
1. a. 
   b. 

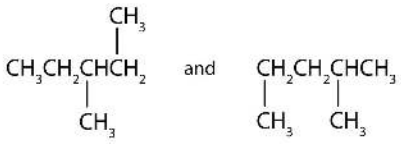
3. a. cyclopentyl bromide
   b. cyclohexyl chloride

12.10: Chapter Summary

Additional Exercises

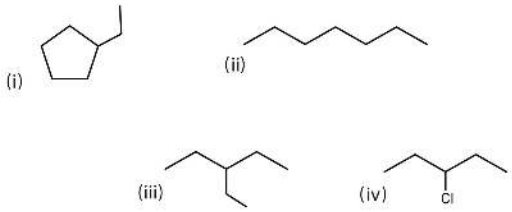
1. You find an unlabeled jar containing a solid that melts at 48°C. It ignites readily and burns readily. The substance is insoluble in water and floats on the surface. Is the substance likely to be organic or inorganic?
2. Give the molecular formulas for methylcyclopentane, 2-methylpentane, and cyclohexane. Which are isomers?
3. What is wrong with each name? (Hint: first write the structure *as if* it were correct.) Give the correct name for each compound.
   a. 2-dimethylpropane
   b. 2,3,3-trimethylbutane
   c. 2,4-diethylpentane
   d. 3,4-dimethyl-5-propylhexane
4. What is the danger in swallowing a liquid alkane?
5. Distinguish between lighter and heavier liquid alkanes in terms of their effects on the skin.
6. Following is the line formula for an alkane. Draw its structure and give its name.



7. Write equations for the complete combustion of each compound.
   a. propane (a bottled gas fuel)
   b. octane (a typical hydrocarbon in gasoline).
8. The density of a gasoline sample is 0.690 g/mL. On the basis of the complete combustion of octane, calculate the amount in grams of carbon dioxide (CO_2) and water (H_2O) formed per gallon (3.78 L) of the gasoline when used in an automobile.
9. Draw the structures for the five isomeric hexanes (C_6H_{14}). Name each by the IUPAC system.
10. Indicate whether the structures in each set represent the same compound or isomers.
    a. 
    b. 

c. 

11. Consider the line-angle formulas shown here and answer the questions.



a. Which pair of formulas represents isomers? Draw each structure.
b. Which formula represents an alkyl halide? Name the compound and write its condensed structural formula.
c. Which formula represents a cyclic alkane? Name the compound and draw its structure.
d. What is the molecular formula of the compound represented by (i)?

Answers

1. organic

3.

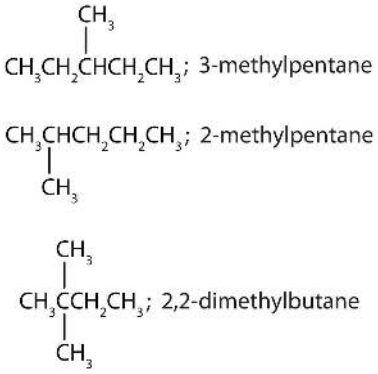
a. Two numbers are needed to indicate two substituents; 2,2-dimethylpropane.
b. The lowest possible numbers were not used; 2,2,3-trimethylbutane.
c. An ethyl substituent is not possible on the second carbon atom; 3,5-dimethylheptane.
d. A propyl substituent is not possible on the fifth carbon atom; 3,4,5-trimethyloctane.

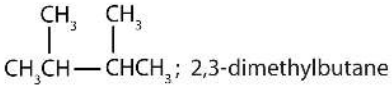
5. Lighter alkanes wash away protective skin oils; heavier alkanes form a protective layer.

7.

a. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
b. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

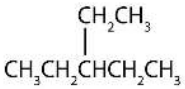
9. $CH_3CH_2CH_2CH_2CH_2CH_3$; hexane





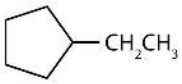
11.

a. ii and iii; $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ and



b. iv; 3-chloropentane; $CH_3CH_2CHClCH_2CH_3$

c. i; ethylcyclopentane;



d. C_7H_{14}

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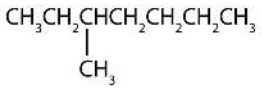
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10.E: Unsaturated and Aromatic Hydrocarbons (Exercises)

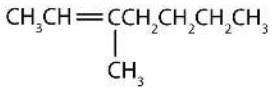
13.1: Alkenes- Structures and Names

Concept Review Exercises

1. Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon.
2. Briefly identify the important distinctions between an alkene and an alkane.
3. Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne.

a. 

b. $CH_3CH_2C{\equiv}CCH_3$

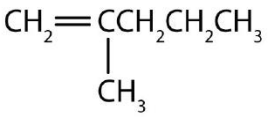
c. 

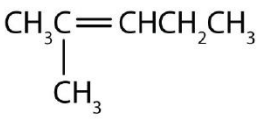
Answers

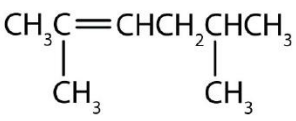
1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
2. An alkene has a double bond; an alkane has single bonds only.
3. a. saturated; alkane
   b. unsaturated; alkyne
   c. unsaturated; alkene

Exercises

1. Draw the structure for each compound.
   a. 2-methyl-2-pentene
   b. 2,3-dimethyl-1-butene
   c. cyclohexene
2. Draw the structure for each compound.
   a. 5-methyl-1-hexene
   b. 3-ethyl-2-pentene
   c. 4-methyl-2-hexene
3. Name each compound according to the IUPAC system.

a. 

b. 

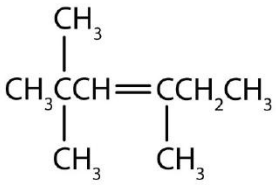
c. 

4. Name each compound according to the IUPAC system.

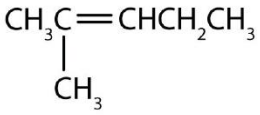


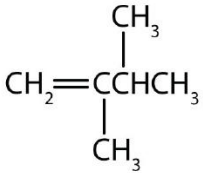
a. 

b.

c. 

Answers

1. a. 

b. 

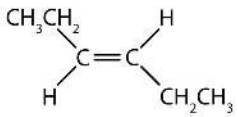
c. 

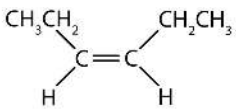
3. a. 2-methyl-1-pentene
   b. 2-methyl-2-pentene
   c. 2,5-dimethyl-2-hexene

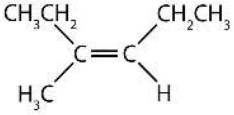
13.2: Cis-Trans Isomers (Geometric Isomers)

Concept Review Exercises

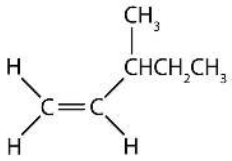
1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.

a. 

b. 

c. 

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d. 

Answers

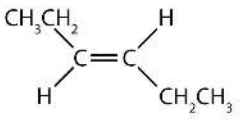
1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.
2. a. trans (the two hydrogen atoms are on opposite sides)
   b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
   c. cis (the two ethyl groups are on the same side)
   d. neither (flipping the bond does not change the molecule. There are no isomers for this molecule)

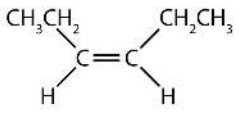
Exercises

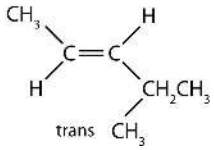
1. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene
   d. 1,1-dibromo-1-butene
   e. 2-butenoic acid ($CH_3CH=CHCOOH$)
2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2,3-dimethyl-2-pentene
   b. 1,1-dimethyl-2-ethylcyclopropane
   c. 1,2-dimethylcyclohexane
   d. 5-methyl-2-hexene
   e. 1,2,3-trimethylcyclopropane

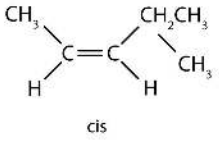
Answer

1. a: none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).
   b:

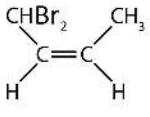

cis


trans

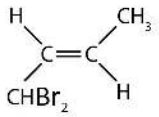
c: 
trans


cis

d:

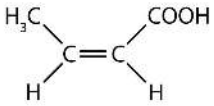


cis

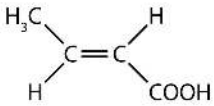


trans

e:



cis



trans

13.3: Physical Properties of Alkenes

Concept Review Exercises

1. Briefly describe the physical properties of alkenes. How do these properties compare to those of the alkanes?
2. Without consulting tables, arrange the following alkenes in order of increasing boiling point: 1-butene, ethene, 1-hexene, and propene.

Answers

1. Alkenes have physical properties (low boiling points, insoluble in water) quite similar to those of their corresponding alkanes.
2. ethene < propene < 1-butene < 1-hexene

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
   a. 1-pentene or 1-butene
   b. 3-heptene or 3-nonene
2. Which is a good solvent for cyclohexene, pentane or water?

Answer

1. a. 1-pentene
   b. 3-nonene

13.4: Chemical Properties of Alkenes

Concept Review Exercises

1. What is the principal difference in properties between alkenes and alkanes? How are they alike?
2. If $C_{12}H_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product?

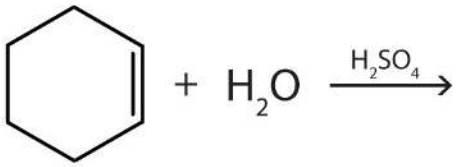
Answers

1. Alkenes undergo addition reactions; alkanes do not. Both burn.
2. $C_{12}H_{24}Br_2$

Exercises

1. Complete each equation.
   a. $(CH_3)_2C{=}CH_2 + Br_2 \rightarrow$
   b. $CH_2{=}C(CH_3)CH_2CH_3 + H_2 \xrightarrow{Ni}$

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c.

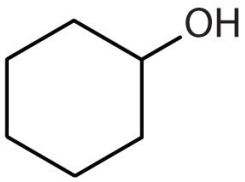
2. Complete each equation.
   a. $CH_2{=}CHCH{=}CH_2 + 2H_2 \xrightarrow{Ni}$
   b. $(CH_3)_2C{=}C(CH_3)_2 + H_2O \xrightarrow{H_2SO_4}$



c.

Answer

1. a. $(CH_3)_2CBrCH_2Br$
   b. $CH_3CH(CH_3)CH_2CH_3$



c.

13.5: Polymers

Concept Review Exercises

1. What is a monomer? What is a polymer? How do polymer molecules differ from the molecules we have discussed in earlier sections of this chapter?
2. What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?
3. What is the molecular formula of a polymer molecule formed by the addition polymerization of 175 molecules of vinyl chloride ($CH_2{=}CHCl$)?

Answers

1. Monomers are small molecules that can be assembled into giant molecules referred to as polymers, which are much larger than the molecules we discussed earlier in this chapter.
2. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers.
3. $C_{350}H_{525}Cl_{175}$

Exercises

1. Write the condensed structural formula of the monomer from which Saran is formed. A segment of the Saran molecule has the following structure: $CH_2CCl_2CH_2CCl_2CH_2CCl_2CH_2CCl_2$.
2. Write the condensed structural formula for the section of a molecule formed from four units of the monomer $CH_2{=}CHF$.

Answer

1. $H_2C{=}CCl_2$

13.6: Alkynes

Concept Review Exercises

1. Briefly identify the important differences between an alkene and an alkyne. How are they similar?
2. The alkene $(CH_3)_2CHCH_2CH{=}CH_2$ is named 4-methyl-1-pentene. What is the name of $(CH_3)_2CHCH_2C{\equiv}CH$?
3. Do alkynes show cis-trans isomerism? Explain.

Answers

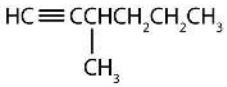
1. Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.
2. 4-methyl-1-pentyne
3. No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

Exercises

1. Draw the structure for each compound.
   a. acetylene
   b. 3-methyl-1-hexyne
2. Draw the structure for each compound.
   a. 4-methyl-2-hexyne
   b. 3-octyne
3. Name each alkyne.
   a. $CH_3CH_2CH_2C{\equiv}CH$
   b. $CH_3CH_2CH_2C{\equiv}CCH_3$

Answers

1. a. H–C≡C–H

   b. 

3. a. 1-pentyne
   b. 2-hexyne

13.7: Aromatic Compounds- Benzene

Concept Review Exercises

1. How do the typical reactions of benzene differ from those of the alkenes?
2. Briefly describe the bonding in benzene.
3. What does the circle mean in the chemist's representation of benzene?

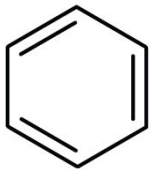
Answers

1. Benzene is rather unreactive toward addition reactions compared to an alkene.
2. Valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized).
3. The six electrons are shared equally by all six carbon atoms.

Exercises

1. Draw the structure of benzene as if it had alternate single and double bonds.
2. Draw the structure of benzene as chemists usually represent it today.

Answer

1. 

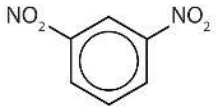
13.8: Structure and Nomenclature of Aromatic Compounds

Concept Review Exercises

1. Briefly identify the important characteristics of an aromatic compound.
2. What is meant by the prefixes *meta*, *ortho*, or *para*? Give the name and draw the structure for a compound that illustrates each.
3. What is a phenyl group? Give the structure for 3-phenyloctane.

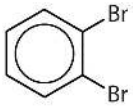
Answers

1. An aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties.
2. meta = 1,3 disubstitution; (answers will vary)



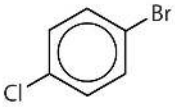
m-dinitrobenzene or 1,3-dinitrobenzene

ortho = 1,2 disubstitution



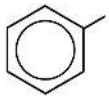
o-dibromobenzene or 1,2-dibromobenzene

para = 1,4 disubstitution or 1-bromo-4-chlorobenzene

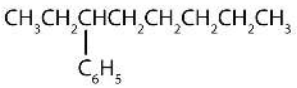


p-bromochlorobenzene or 1-bromo-2-chlorobenzene

3. phenyl group: C_6H_5 or

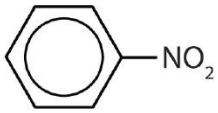


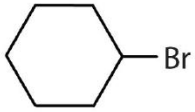
3-phenyloctane:



Exercises

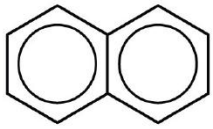
1. Is each compound aromatic?

a. 

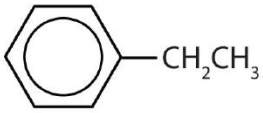
b. 

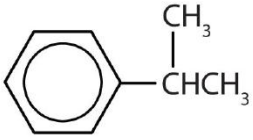
2. Is each compound aromatic?

a. 

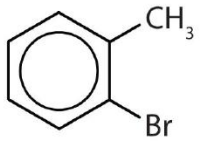
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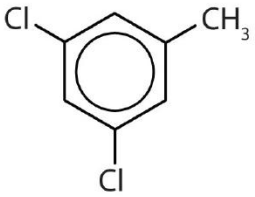
3. Draw the structure for each compound.
   a. toluene
   b. *m*-diethylbenzene
   c. 3,5-dinitrotoluene
4. Draw the structure for each compound.
   a. *p*-dichlorobenzene
   b. naphthalene
   c. 1,2,4-trimethylbenzene
5. Name each compound with its IUPAC name.

a. 

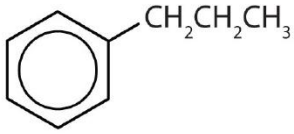
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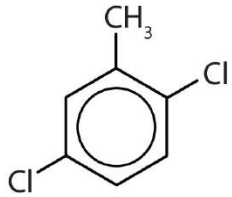
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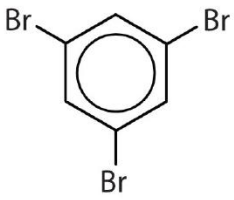
c. 

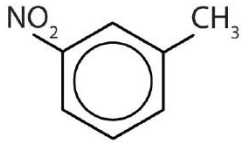
d. 

6. Name each compound with its IUPAC name.

a. 

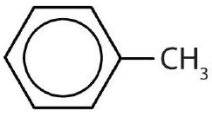
b. 

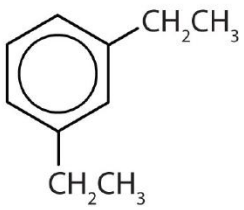
c. 

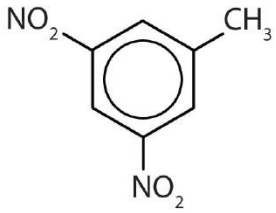
d. 

Answers

1. a. yes
   b. no

3. a. 

b. 

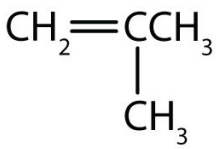


c.

5. a. ethylbenzene
   b. isopropylbenzene
   c. *o*-bromotoluene
   d. 3,5-dichlorotoluene

Additional Exercises

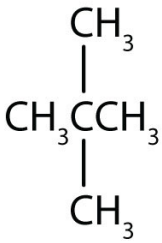
1. Classify each compound as saturated or unsaturated.



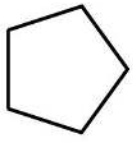
a.

b. $CH_3C{\equiv}CCH_3$

2. Classify each compound as saturated or unsaturated.

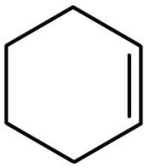


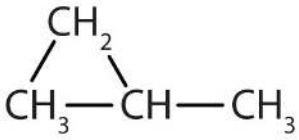
a.



b.

3. Give the molecular formula for each compound.

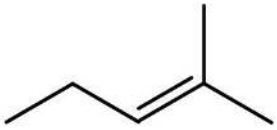
a. 

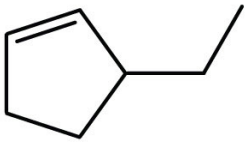
b. 

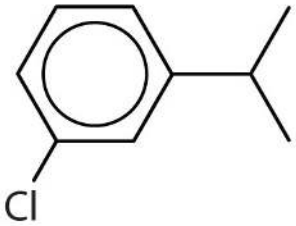
4. When three isomeric pentenes—X, Y, and Z—are hydrogenated, all three form 2-methylbutane. The addition of Cl_2 to Y gives 1,2-dichloro-3-methylbutane, and the addition of Cl_2 to Z gives 1,2-dichloro-2-methylbutane. Draw the original structures for X, Y, and Z.
5. Pentane and 1-pentene are both colorless, low-boiling liquids. Describe a simple test that distinguishes the two compounds. Indicate what you would observe.
6. Draw and name all the alkene cis-trans isomers corresponding to the molecular formula C_5H_{10}. (Hint: there are only two.)
7. The complete combustion of benzene forms carbon dioxide and water:

   $C_6H_6 + O_2 \rightarrow CO_2 + H_2O$

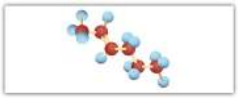
   Balance the equation. What mass, in grams, of carbon dioxide is formed by the complete combustion of 39.0 g of benzene?
8. Describe a physiological effect of some PAHs.
9. What are some of the hazards associated with the use of benzene?
10. What is wrong with each name? Draw the structure and give the correct name for each compound.
    a. 2-methyl-4-heptene
    b. 2-ethyl-2-hexene
    c. 2,2-dimethyl-3-pentene
11. What is wrong with each name?
    a. 2-bromobenzene
    b. 3,3-dichlorotoluene
    c. 1,4-dimethylnitrobenzene
12. Following are line-angle formulas for three compounds. Draw the structure and give the name for each.

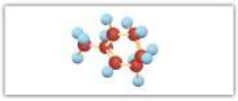
a. 

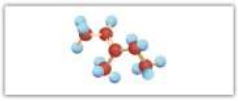
b. 

c. 

13. Following are ball-and-stick molecular models for three compounds (blue balls represent H atoms; red balls are C atoms). Write the condensed structural formula and give the name for each.

a. 

b. 

c. 

Answers

1.

a. unsaturated
b. unsaturated

3.

a. C_6H_{10}
b. C_4H_8

5. Add bromine solution (reddish-brown) to each. Pentane will not react, and the reddish-brown color persists; 1-pentene will react, leaving a colorless solution.

7. $2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$; 132 g

9. carcinogenic, flammable

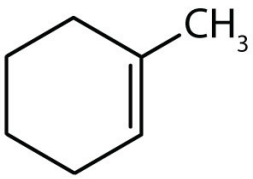
11.

a. number not needed
b. can’t have two groups on one carbon atom on a benzene ring
c. can’t have a substituent on the same carbon atom as the nitro group

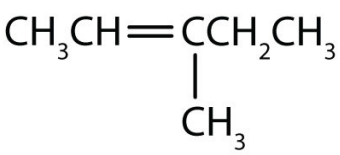
13.

a. $CH_3CH{=}CHCH_2CH_2CH_3$; 2-hexene

b.



c.



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10.S: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.

Organic chemistry is the chemistry of carbon compounds, and **inorganic chemistry** is the chemistry of all the other elements. Carbon atoms can form stable covalent bonds with other carbon atoms and with atoms of other elements, and this property allows the formation the tens of millions of organic compounds. **Hydrocarbons** contain only hydrogen and carbon atoms.

Hydrocarbons in which each carbon atom is bonded to four other atoms are called **alkanes** or **saturated hydrocarbons**. They have the general formula C_nH_{2n+2}. Any given alkane differs from the next one in a series by a CH_2 unit. Any family of compounds in which adjacent members differ from each other by a definite factor is called a **homologous series**.

Carbon atoms in alkanes can form straight chains or branched chains. Two or more compounds having the same molecular formula but different structural formulas are **isomers** of each other. There are no isomeric forms for the three smallest alkanes; beginning with C_4H_{10}, all other alkanes have isomeric forms.

A **structural formula** shows all the carbon and hydrogen atoms and how they are attached to one another. A **condensed structural formula** shows the hydrogen atoms right next to the carbon atoms to which they are attached. A **line-angle formula** is a formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

The **IUPAC System of Nomenclature** provides rules for naming organic compounds. An **alkyl group** is a unit formed by removing one hydrogen atom from an alkane.

The physical properties of alkanes reflect the fact that alkane molecules are nonpolar. Alkanes are insoluble in water and less dense than water.

Alkanes are generally unreactive toward laboratory acids, bases, oxidizing agents, and reducing agents. They do burn (undergo **combustion reactions**).

Alkanes react with halogens by substituting one or more halogen atoms for hydrogen atoms to form **halogenated hydrocarbons**. An **alkyl halide (haloalkane)** is a compound resulting from the replacement of a hydrogen atom of an alkane with a halogen atom.

Cycloalkanes are hydrocarbons whose molecules are closed rings rather than straight or branched chains. A **cyclic hydrocarbon** is a hydrocarbon with a ring of carbon atoms

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10.S: Unsaturated and Aromatic Hydrocarbons (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Any hydrocarbon containing either a double or triple bond is an **unsaturated hydrocarbon**. **Alkenes** have a carbon-to-carbon double bond. The general formula for alkenes with one double bond is C_nH_{2n}. Alkenes can be straight chain, branched chain, or cyclic. Simple alkenes often have common names, but all alkenes can be named by the system of the International Union of Pure and Applied Chemistry.

Cis-trans isomers (or geometric isomers) are characterized by molecules that differ only in their configuration around a rigid part of the structure, such as a carbon–to-carbon double bond or a ring. The molecule having two identical (or closely related) atoms or groups on the same side is the **cis isomer**; the one having the two groups on opposite sides is the **trans isomer**.

The physical properties of alkenes are quite similar to those of alkanes. Like other hydrocarbons, alkenes are insoluble in water but soluble in organic solvents.

More reactive than alkanes, alkenes undergo **addition reactions** across the double bond:

- Addition of hydrogen (**hydrogenation**):

$$CH_2=CH_2 + H_2 \rightarrow CH_3CH_3$$

- Addition of halogen (**halogenation**):

$$CH_2=CH_2 + X_2 \rightarrow XCH_2CH_2X$$

  where X = F, Cl, Br, or I.

- Addition of water (**hydration**):

$$CH_2=CH_2 + HOH \rightarrow HCH_2CH_2OH$$

Alkenes also undergo **addition polymerization**, molecules joining together to form long-chain molecules.

$$\ldots CH_2=CH_2 + CH_2=CH_2 + CH_2=CH_2 + \ldots \rightarrow \ldots CH_2CH_2–CH_2CH_2–CH_2CH_2–\ldots$$

The reactant units are **monomers**, and the product is a **polymer**.

Alkynes have a carbon-to-carbon triple bond. The general formula for alkynes is $C_nH_{2n\,-\,2}$. The properties of alkynes are quite similar to those of alkenes. They are named much like alkenes but with the ending *-yne*.

The cyclic hydrocarbon *benzene* (C_6H_6) has a ring of carbon atoms. The molecule seems to be unsaturated, but it does not undergo the typical reactions expected of alkenes. The electrons that might be fixed in three double bonds are instead *delocalized* over all six carbon atoms.

A hydrocarbon containing one or more benzene rings (or other similarly stable electron arrangements) is an **aromatic hydrocarbon**, and any related substance is an **aromatic compound**. One or more of the hydrogen atoms on a benzene ring can be replaced by other atoms. When two hydrogen atoms are replaced, the product name is based on the relative position of the replacement atoms (or atom groups). A 1,2-disubstituted benzene is designated as an *ortho* (*o*-) isomer; 1,3-, a *meta* (*m*-) isomer; and 1,4-, a *para* (*p*-) isomer. An aromatic group as a substituent is called an **aryl** group.

A **polycyclic aromatic hydrocarbon (PAH)** has fused benzene rings sharing a common side.

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CHAPTER OVERVIEW

11: Alcohols, Thiols, Aldehydes, and Ketones

11.1: Prelude to Organic Compounds of Oxygen
11.2: Organic Compounds with Functional Groups
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11.4: Physical Properties of Alcohols
11.5: Reactions that Form Alcohols
11.6: Reactions of Alcohols
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11.9: Aldehydes and Ketones- Structure and Names
11.10: Properties of Aldehydes and Ketones
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11.E: Organic Compounds of Oxygen (Exercises)
11.S: Organic Compounds of Oxygen (Summary)

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11.1: Prelude to Organic Compounds of Oxygen

One of the more familiar chemical compounds on Earth is ethyl alcohol (ethanol). As the intoxicant in alcoholic beverages, ethanol is often simply called alcohol. If ethanol is diluted, as it is in wine, beer, or mixed drinks with about 1 oz of liquor, and if it is consumed in small quantities, it is relatively safe. In excess—four or more drinks in a few hours—it causes intoxication, which is characterized by a loss of coordination, nausea and vomiting, and memory blackouts.

Excessive ingestion of ethanol over a long period of time leads to cirrhosis of the liver, alteration of brain cell function, nerve damage, and strong physiological addiction. Alcoholism—an addiction to ethanol—is the most serious drug problem in the United States. Heavy drinking shortens a person's life span by contributing to diseases of the liver, the cardiovascular system, and virtually every other organ of the body.

In small quantities—one or two drinks a day—ethanol might promote health. In addition to the possible benefits of modest amounts of ethanol, a chemical in red wines, resveratrol, is thought to lower the risk of heart disease. Resveratrol, found in red grapes, is an antioxidant. It inhibits the oxidation of cholesterol and subsequent clogging of the arteries. One need not drink wine to get the benefits of resveratrol, however. It can be obtained by eating the grapes or drinking red grape juice.

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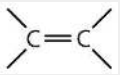
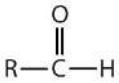
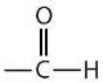
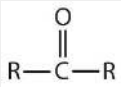
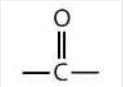
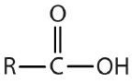
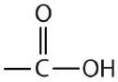
11.2: Organic Compounds with Functional Groups

Learning Objectives

- to describe functional groups and explain why they are useful in the study of organic chemistry.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of organic compound families. Each family is based on a common, simple functional group that contains an oxygen atom or a nitrogen atom. Some common functional groups are listed in Table **11.2.1**.

Table **11.2.1**: Selected Organic Functional Groups

Name of Family	General Formula	Functional Group	Suffix*
alkane	RH	none	*-ane*
alkene	$R_2C{=}CR_2$		*-ene*
alkyne	RC≡CR	–C≡C–	*-yne*
alcohol	ROH	–OH	*-ol*
thiol	RSH	–SH	*-thiol*
ether	ROR	–O–	ether
aldehyde			*-al*
ketone			*-one*
carboxylic acid			*-oic acid*

*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

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11.3: Alcohols - Nomenclature and Classification

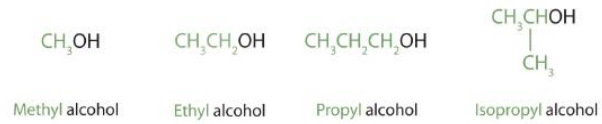
Learning Objectives

- 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:

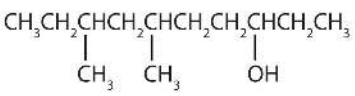
1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the 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 **11.3.1** shows 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 **11.3.1**: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Example 11.3.1

Give the IUPAC name for each compound.

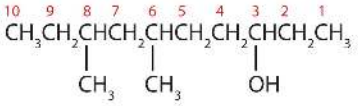
a. 

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.

- $HOCH_2CH_2CH_2CH_2CH_2OH$

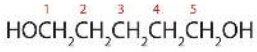
Solution

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).



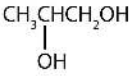
The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH_3) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

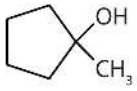
b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



? Exercise 11.3.1

Give the IUPAC name for each compound.

a. 

- 

✔ Example 11.3.2

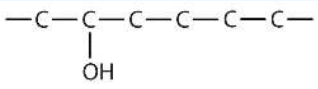
Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

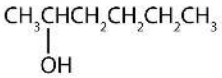
Solution

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–.

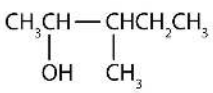
The 2 indicates that the OH group is attached to the second carbon atom.



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 11.3.2

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.

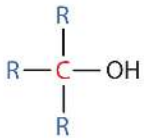
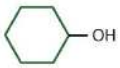


Table **11.3.1** names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Table **11.3.1**: 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
$CH_3CH_2CHOHCH_3$	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.

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11.4: Physical Properties of Alcohols

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 **11.4.1**).

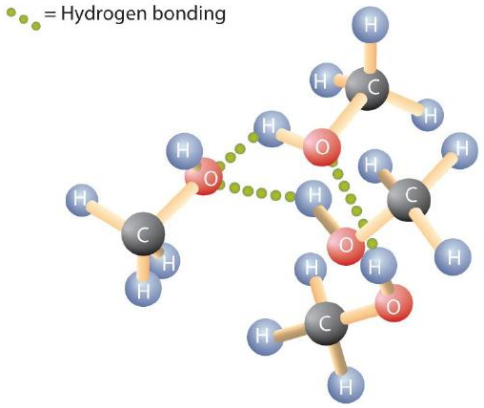


Figure **11.4.1**: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table **11.4.1** 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 **11.4.1**: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	–164
HOH	water	18	100
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 **11.4.2**). 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.

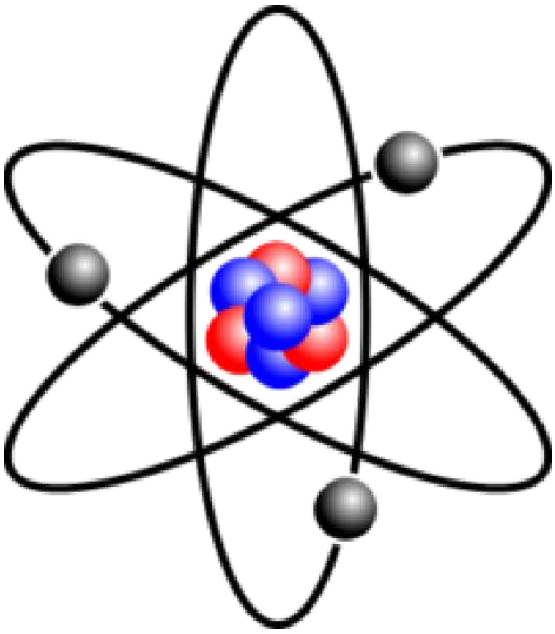


Figure **11.4.2**: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

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.

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11.5: Reactions that Form Alcohols

Learning Objectives

- To describe how to prepare alcohols from alkenes

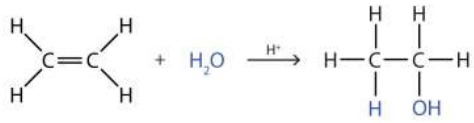
Methanol is prepared by combining hydrogen gas and carbon monoxide at high temperatures and pressures in the presence of a catalyst composed of zinc oxide (ZnO) and chromium oxide (Cr_2O_3) catalyst:

$$2H_2 + CO \xrightarrow[ZnO,\ Cr_2O_3]{200\ atm,\ 350°C} CH_3OH$$

Methanol is an important solvent and is used as an automotive fuel, either as the pure liquid—as in some racing cars—or as an additive in gasoline.

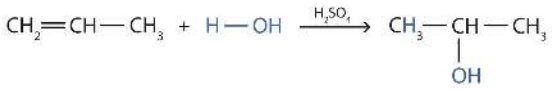
> *Nearly 2 billion gallons of methanol are produced each year in the United States by the catalytic reduction of carbon monoxide with hydrogen gas.*

Many simple alcohols are made by the hydration of alkenes. Ethanol is made by the hydration of ethylene in the presence of a catalyst such as sulfuric acid (H_2SO_4).



Ethylene Water Ethanol

In a similar manner, isopropyl alcohol is produced by the addition of water to propene (propylene).



Propylene Isopropyl alcohol (2-propanol)

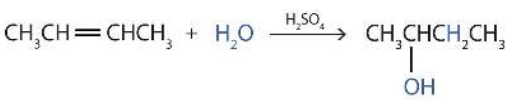
Additional Exercise **11.5.1** describes how to use a generalization called Markovnikov's rule to predict the results when the addition of water to an alcohol has two possible products.

Example 11.5.1

Write the equation for the reaction of 2-butene with water to form 2-butanol. Indicate that sulfuric acid is used as a catalyst.

Solution

First write the condensed structural formula of 2-butene and indicate that it reacts with water. Then write the condensed structural formula of 2-butanol after the reaction arrow to indicate that it is the product. Finally, write the formula for the catalyst above the arrow.



Exercise 11.5.1

Write the equation for the reaction of cyclopentene with water to form cyclopentanol. Indicate that phosphoric acid (H_3PO_4) is used as a catalyst.

> *Many OH compounds in living systems are formed by alkene hydration. Here is an example that occurs in the Krebs cycle: fumarate is hydrated to form malate.*
>
> $$^-OOCCH{=}CHCOO^- + HOH \overset{\text{enzyme}}{\rightleftharpoons} {}^-OOCCH_2CHOHCOO^-$$

In addition to its preparation from ethylene, ethanol is made by the fermentation of sugars or starch from various sources (potatoes, corn, wheat, rice, etc.). Fermentation is catalyzed by enzymes found in yeast and proceeds by an elaborate multistep mechanism. We can represent the overall process as follows:

$$(C_6H_{10}O_5)_x \xrightarrow{\text{enzymes}} C_6H_{12}O_6 \xrightarrow{\text{enzymes}} 2CH_3CH_2OH + 2CO_2$$

Starch — Glucose — Ethanol

To Your Health: The Physiological Effects of Alcohols

Methanol is quite poisonous to humans. Ingestion of as little as 15 mL of methanol can cause blindness, and 30 mL (1 oz) can cause death. However, the usual fatal dose is 100 to 150 mL. The main reason for methanol's toxicity is that we have liver enzymes that catalyze its oxidation to formaldehyde, the simplest member of the aldehyde family:

$$CH_3OH \xrightarrow{\text{liver enzymes}} H{-}\overset{\overset{O}{\|}}{C}{-}H$$

Methanol — Formaldehyde

Formaldehyde reacts rapidly with the components of cells, coagulating proteins in much the same way that cooking coagulates an egg. This property of formaldehyde accounts for much of the toxicity of methanol.

Organic and biochemical equations are frequently written showing only the organic reactants and products. In this way, we focus attention on the organic starting material and product, rather than on balancing complicated equations.

Ethanol is oxidized in the liver to acetaldehyde:

$$CH_3CH_2OH \xrightarrow{\text{liver enzymes}} CH_3{-}\overset{\overset{O}{\|}}{C}{-}H$$

Ethanol — Acetaldehyde

The acetaldehyde is in turn oxidized to acetic acid ($HC_2H_3O_2$), a normal constituent of cells, which is then oxidized to carbon dioxide and water. Even so, ethanol is potentially toxic to humans. The rapid ingestion of 1 pt (about 500 mL) of pure ethanol would kill most people, and acute ethanol poisoning kills several hundred people each year—often those engaged in some sort of drinking contest. Ethanol freely crosses into the brain, where it depresses the respiratory control center, resulting in failure of the respiratory muscles in the lungs and hence suffocation. Ethanol is believed to act on nerve cell membranes, causing a diminution in speech, thought, cognition, and judgment.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol. It has a high vapor pressure, and its rapid evaporation from the skin produces a cooling effect. It is toxic when ingested but, compared to methanol, is less readily absorbed through the skin.

Summary

Many alcohols are made by the hydration of alkenes. Ethanol can be made by the fermentation of sugars or starch from various sources.

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11.6: Reactions of Alcohols

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 **11.6.1**, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

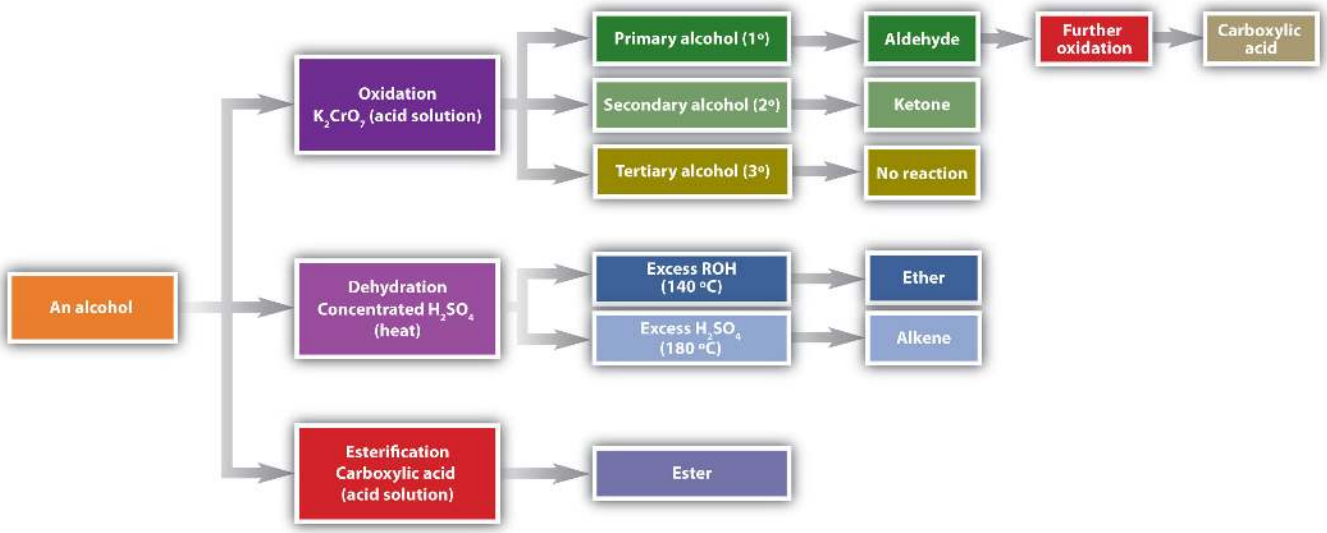
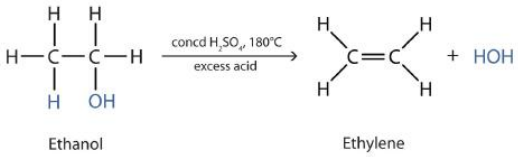


Figure **11.6.1**: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

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.

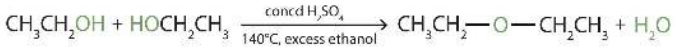
Dehydration

As noted in Figure **11.6.1**, 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:



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.

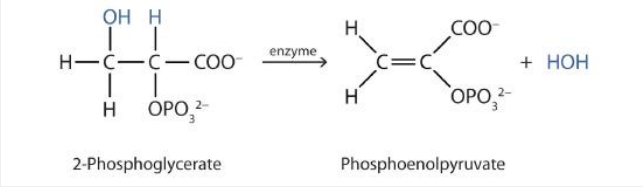
Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.



Two molecules of ethanol 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

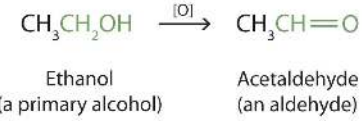


Structural formula of 2 phosphoglycerate forming phosphoenolpyruvate and a water molecule with the aid of enzymes.

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.

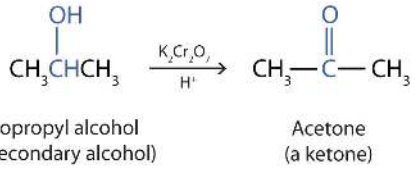
Oxidation

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:

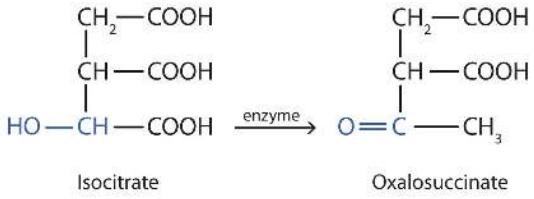


Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group 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:



Isocitrate Oxalosuccinate

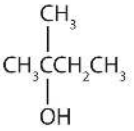
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

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.

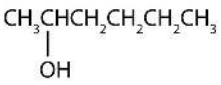
Example 11.6.1

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.

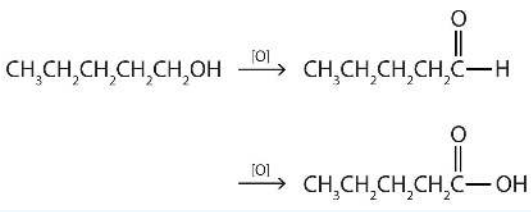
c. 

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

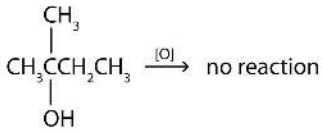
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

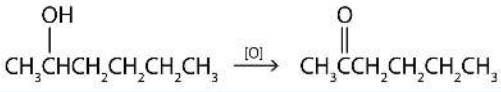
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



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.



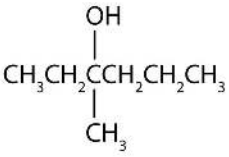
c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.



? Exercise 11.6.1

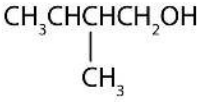
Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

a.



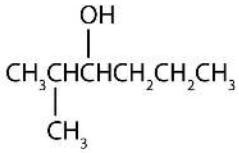
From left to right, there are six carbons on the alkane straight chain with a hydroxyl group and methyl group on carbon 3.

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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11.7: Phenols

Learning Objectives

- To describe the structure and uses of some phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

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

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive ("hospital smell") odor.

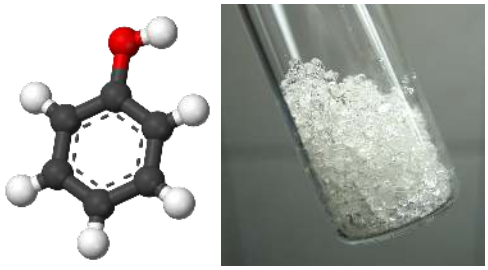


Figure 11.7.1: (Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. from Wikipedia

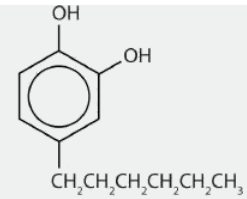
To Your Health: Phenols and Us

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.



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

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

Summary

Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

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11.8: 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 **11.8.1**).

Table **11.8.1**: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

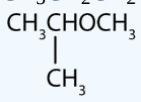
Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	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 11.8.1

What is the common name for each ether?

a. $CH_3CH_2CH_2OCH_2CH_2CH_3$

b. 

Solution

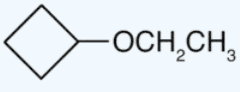
a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.

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 11.8.1

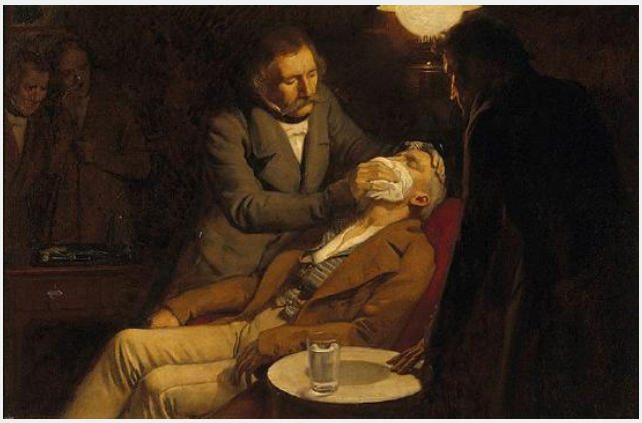
What is the common name for each ether?

a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$

b. 

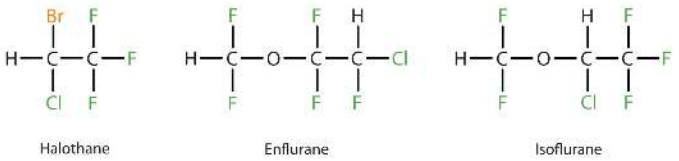
To Your Health: Ethers as General Anesthetics

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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11.9: Aldehydes and Ketones- Structure and Names

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.

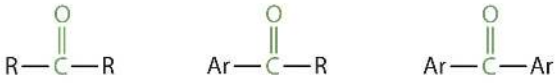
The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.



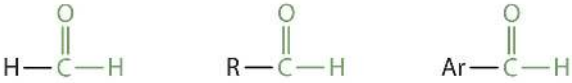
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *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).



An aldehyde

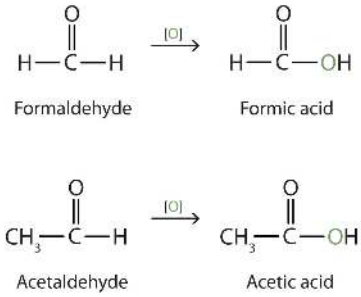


A ketone

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

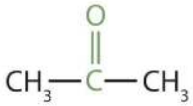
Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.



The stems for the common names of the first four aldehydes are as follows:

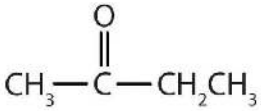
- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

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

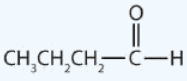
Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

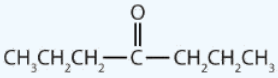


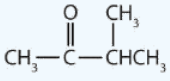
Ethyl methyl ketone

Example 11.9.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

a. 

b. 

c. 

Solution

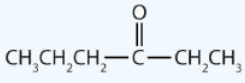
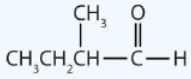
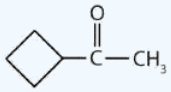
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

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 11.9.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

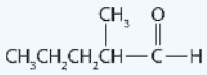
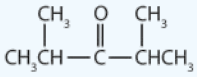
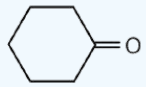
1. 
2. 
3. 

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 11.9.2

Give the IUPAC name for each compound.

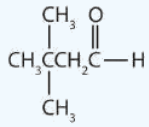
a. 
b. 
c. 

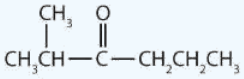
Solution

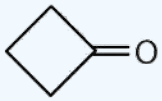
a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom 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. 

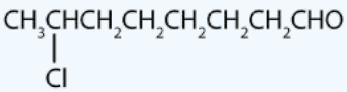
Example 11.9.3

Draw the structure for each compound.

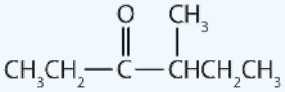
a. 7-chlorooctanal
b. 4-methyl–3-hexanone

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 11.9.3

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.

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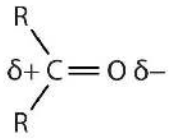
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11.10: Properties of Aldehydes and Ketones

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 **11.10.1** shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

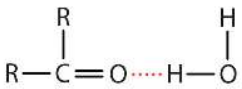
Table **11.10.1**: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

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.

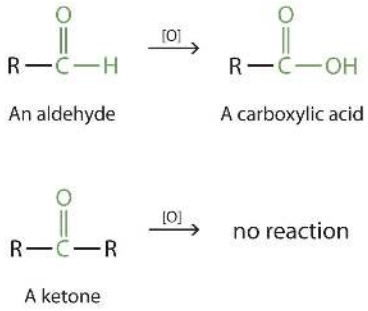
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.



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 11.10.1). Ordinary ketones do not react with Tollens' reagent.



Figure 11.10.1: 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 **11.10.2**).

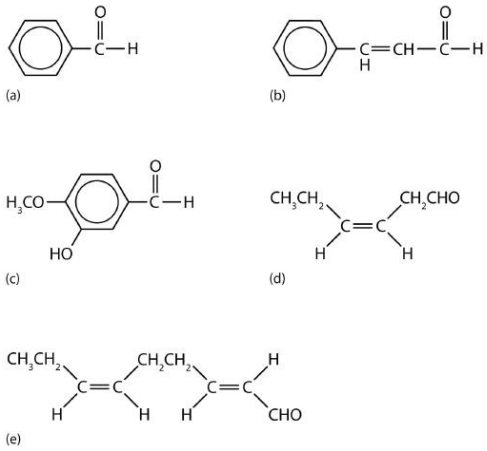


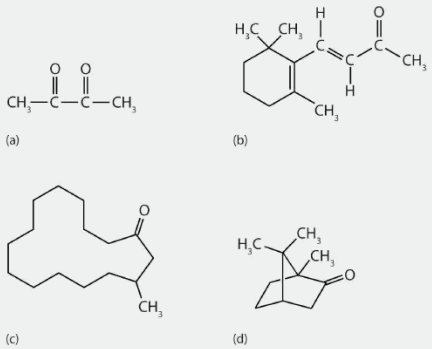
Figure **11.10.2** Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

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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11.11: Organic Sulfur Compounds

Learning Objectives

- Identify thiols (mercaptans) by the presence of an SH group.
- The mild oxidation of thiols gives disulfides.

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. Thiols (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula CH_3SH. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called **disulfides**.

$$2RSH \xrightarrow{[O]} RSSR$$

The amino acids cysteine [$HSCH_2CH(NH_2)COOH$] and methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$] contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

Thioethers, which are sulfur analogs of ethers, have the form general formula RSR′. An example is dimethylsulfide (CH_3SCH_3), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

Career Focus: Paramedic

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the “father” of shock trauma medicine, serves as the motto for many paramedic units: “Next to creating a life the finest thing a man can do is save one.” —Abraham Lincoln

Summary

Thiols, thioethers, and disulfides are common in biological compounds.

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11.E: Organic Compounds of Oxygen (Exercises)

14.1: Organic Compounds with Functional Groups

Concept Review Exercises

1. What is the functional group of an alkene? An alkyne?
2. Does $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ have a functional group? Explain.

Answers

1. carbon-to-carbon double bond; carbon-to-carbon triple bond
2. No; it has nothing but carbon and hydrogen atoms and all single bonds.

Exercises

1. What is the functional group of 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. What is the functional group of butyl bromide, $CH_3CH_2CH_2CH_2Br$?

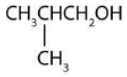
Answer

1. OH

14.2: Alcohols - Nomenclature and Classification

Concept Review Exercises

1. Is isobutyl alcohol primary, secondary, or tertiary? Explain.

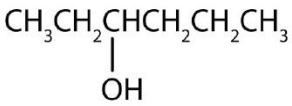
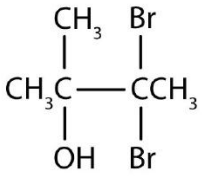
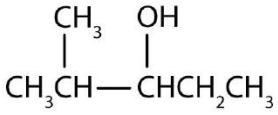


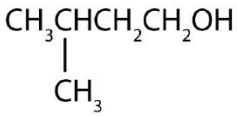
2. What is the LCC in 2-ethyl-1-hexanol? What is taken as the LCC in naming the compound? Explain.

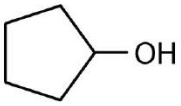
Answers

1. primary; the carbon atom bearing the OH group is attached to only one other carbon atom
2. 7 carbon atoms; the 6-atom chain includes the carbon atom bearing the OH group

Exercises

1. Name each alcohol and classify it as primary, secondary, or tertiary.
   a. $CH_3CH_2CH_2CH_2CH_2CH_2OH$
   b. 
   c. 
2. Name each alcohol and classify it as primary, secondary, or tertiary.
   a. 

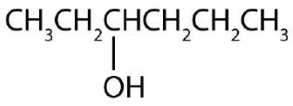
b. 

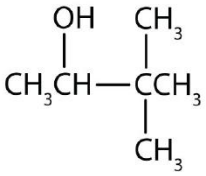
c. 

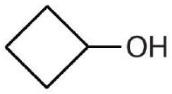
3. Draw the structure for each alcohol.
   a. 3-hexanol
   b. 3,3-dimethyl-2-butanol
   c. cyclobutanol
4. Draw the structure for each alcohol.
   a. cyclopentanol
   b. 4-methyl-2-hexanol
   c. 4,5-dimethyl-3-heptanol

Answers

1. a. 1-hexanol; primary
   b. 3-hexanol; secondary
   c. 3,3-dibromo-2-methyl-2-butanol; tertiary

3. a. 

b. 

c. 

14.3: Physical Properties of Alcohols

Concept Review Exercises

1. Why is ethanol more soluble in water than 1-hexanol?
2. Why does 1-butanol have a lower boiling point than 1-hexanol?

Answers

1. Ethanol has an OH group and only 2 carbon atoms; 1-hexanol has one OH group for 6 carbon atoms and is thus more like a (nonpolar) hydrocarbon than ethanol is.
2. The molar mass of 1-hexanol is greater than that of 1-butanol.

Exercises

Answer the following exercises without consulting tables in the text.

1. Arrange these alcohols in order of increasing boiling point: ethanol, methanol, and 1-propanol.

2. Which has the higher boiling point—butane or 1-propanol?
3. Arrange these alcohols in order of increasing solubility in water: 1-butanol, methanol, and 1-octanol.
4. Arrange these compounds in order of increasing solubility in water: 1-butanol, ethanol, and pentane.

Answers

1. methanol < ethanol < 1-propanol
3. 1-octanol < 1-butanol < methanol

14.4: Reactions that Form Alcohols

Concept Review Exercises

1. Why is methanol more toxic than ethanol?
2. How does rubbing alcohol cool a feverish patient?

Answers

1. Methanol is oxidized to formaldehyde, which destroys tissue; ethanol is oxidized to acetaldehyde and then acetic acid, a normal metabolite.
2. Evaporation removes heat.

Exercises

1. From what alkene is ethanol made? Draw its condensed structural formula.
2. Can methanol be made from an alkene? Explain.

Answer

1. ethylene; $CH_2=CH_2$

14.5: Reactions of Alcohols

Conceptual Questions

1. In a reaction, compound W with the molecular formula $C_4H_{10}O$ is converted to compound X with the formula C_4H_8O. Is W oxidized, reduced, dehydrated, or none of these? Explain.
2. In a reaction, 2 mol of compound Y with the molecular formula $C_4H_{10}O$ is converted to 1 mol of compound Z with the formula $C_8H_{18}O$. Is Y oxidized, reduced, or neither? Explain.

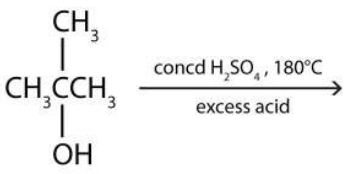
Answers

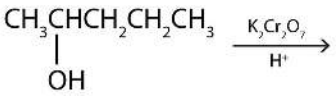
1. oxidized; H is removed
2. neither; water is removed

Exercises

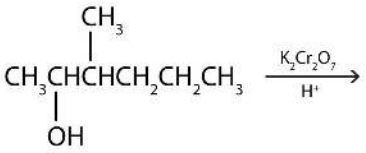
1. Name the three major types of chemical reactions of alcohols.
2. Why do tertiary alcohols not undergo oxidation? Can a tertiary alcohol undergo dehydration?
3. Draw the structure of the product for each reaction.

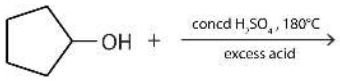
a.



b. 

4. Draw the structure of the product for each reaction.

a. 

b. 

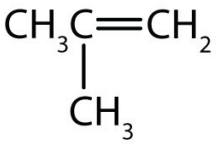
5. Write an equation for the dehydration of 2-propanol to yield each compound type.

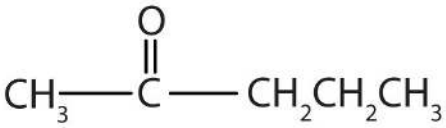
   a. an alkene
   b. an ether

6. Draw the structure of the alkene formed by the dehydration of cyclohexanol.

Answers

1. dehydration, oxidation, and esterification

3. a. 

   b. 

5. a. $\mathrm{CH_3CHOHCH_3} \xrightarrow[\text{180°C, excess acid}]{\text{conc } \mathrm{H_2SO_4}} \mathrm{CH_3COCH_3 + H_2O}$

   b. $\mathrm{2CH_3CHOHCH_3} \xrightarrow[\text{180°C, excess acid}]{\text{conc } \mathrm{H_2SO_4}} \mathrm{(CH_3)_2CHOCH(CH_3)_2 + H_2O}$

14.6: Glycols and Glycerol

Concept Review Exercises

1. In the oxidation of propylene glycol to pyruvic acid, what functional groups in the reactant are involved? What new functional groups appear in the product?
2. Oxalate ion is formed by the oxidation of ethylene glycol. In what kind of reaction is the oxalate ion involved?

Answers

1. two OH groups; a ketone group and a carboxylic acid group
2. precipitation

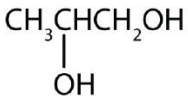
Exercises

1. What is a glycol?
2. Why is ethylene glycol so much more toxic to humans than propylene glycol?

3. Draw the structure for each compound.
   a. 1,5-pentanediol
   b. propylene glycol
4. Draw the structure for each compound.
   a. 1,3-hexandiol
   b. glycerol

Answers

1. an alcohol with two OH groups on adjacent carbon atoms
3. a. $HOCH_2CH_2CH_2CH_2CH_2OH$

   b. 

14.7: Phenols

Concept Review Exercises

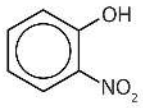
1. How do phenols differ from alcohols in terms of structure and properties?
2. How do phenols differ in properties from aromatic hydrocarbons?

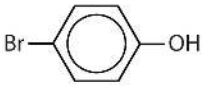
Answers

1. Phenols have an OH group attached directly to an aromatic ring. Phenols are weakly acidic.
2. Phenols have an OH group and are somewhat soluble in water.

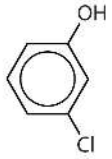
Exercises

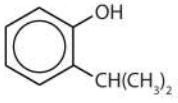
1. Name each compound.

   a. 

   b. 

2. Name each compound.

   a. 

   b. 

3. Draw the structure for each compound.
   a. *m*-iodophenol
   b. *p*-methylphenol (*p*-cresol)

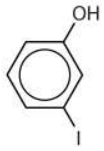
https://chem.libretexts.org/@go/page/490451

4. Draw the structure for each compound.
   a. 2,4,6-trinitrophenol (picric acid)
   b. 3,5-diethylphenol

Answers

1. a. *o*-nitrophenol
   b. *p*-bromophenol

3. a.



   b.



14.8: Ethers

Concept Review Exercises

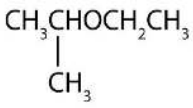
1. Why does diethyl ether ($CH_3CH_2OCH_2CH_3$) have a much lower boiling point than 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. Which is more soluble in water—ethyl methyl ether ($CH_3CH_2OCH_3$) or 1-butanol ($CH_3CH_2CH_2CH_2OH$)? Explain.

Answers

1. Diethyl ether has no intermolecular hydrogen bonding because there is no OH group; 1-butanol has an OH and engages in intermolecular hydrogen bonding.
2. Ethyl methyl ether (three carbon atoms, one oxygen atom) is more soluble in water than 1-butanol (four carbon atoms, one oxygen atom), even though both can engage in hydrogen bonding with water.

Exercises

1. How can ethanol give two different products when heated with sulfuric acid? Name these products.
2. Which of these ethers is isomeric with ethanol—$CH_3CH_2OCH_2CH_3$, $CH_3OCH_2CH_3$, or CH_3OCH_3?
3. Name each compound.
   a. $CH_3OCH_2CH_2CH_3$



   b.

4. Name each compound.
   a. $CH_3CH_2CH_2CH_2OCH_3$
   b. $CH_3CH_2OCH_2CH_2CH_3$
5. Draw the structure for each compound.
   a. methyl ethyl ether
   b. *tert*-butyl ethyl ether
6. Draw the structure for each compound.
   a. diisopropyl ether
   b. cyclopropyl propyl ether

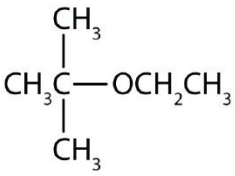
Answers

1. Intramolecular (both the H and the OH come from the same molecule) dehydration gives ethylene; intermolecular (the H comes from one molecule and the OH comes from another molecule) dehydration gives diethyl ether.

3. a. methyl propyl ether
   b. ethyl isopropyl ether

5. a. $CH_3OCH_2CH_3$

   b.

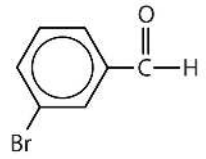


14.9: Aldehydes and Ketones- Structure and Names

Concept Review Exercises

1. Give the structure and IUPAC name for the compound that has the common name m-bromobenzaldehyde.
2. Give the IUPAC name for glyceraldehyde, (HOCH2CHOHCHO). (Hint: as a substituent, the OH group is named hydroxy.)

Answers

1. 

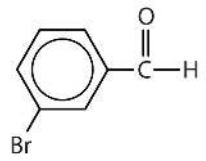
   3-Bromobenzaldehyde

   3-bromobenzaldehyde

2. 2,3-dihydroxypropanal

Answers

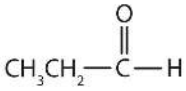
1. The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
2. For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
3. 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.
4. 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.
5. 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.
6. Give the structure and IUPAC name for the compound that has the common name *m*-bromobenzaldehyde.
7. Give the IUPAC name for glyceraldehyde, ($HOCH_2CHOHCHO$). (Hint: as a substituent, the OH group is named *hydroxy*.)

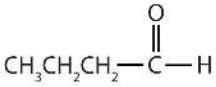
8. 

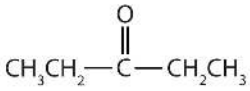
3-Bromobenzaldehyde

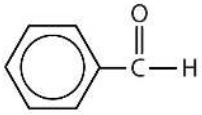
3-bromobenzaldehyde

9. 2,3-dihydroxypropanal
10. Name each compound.

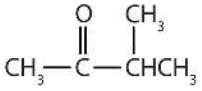
a. 

b. 

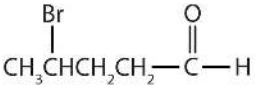
c. 

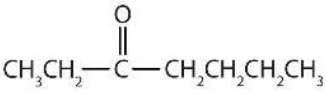
d. 

11. Name each compound.

a. 

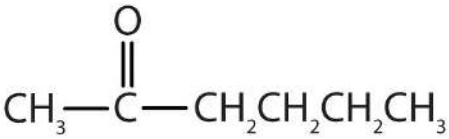
b. $CH_3CH_2CH_2CH_2CH_2CHO$

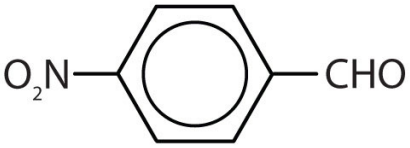
c. 

d. 

12. Draw the structure for each compound.
    a. butyraldehyde
    b. 2-hexanone
    c. *p*-nitrobenzaldehyde
13. Draw the structure for each compound.
    a. 5-ethyloctanal
    b. 2-chloropropanal
    c. 2-hydroxy-3-pentanone
14. a. propanal or propionaldehyde
    b. butanal or butyraldehyde
    c. 3-pentanone or diethyl ketone
    d. benzaldehyde

15. a. $CH_3CH_2CH_2CHO$

b. 

c. 

14.10: Properties of Aldehydes and Ketones

Concept Review Exercises

1. What feature of their structure makes aldehydes easier to oxidize than ketones?
2. How does the carbon-to-oxygen bond of aldehydes and ketones differ from the carbon-to-carbon bond of alkenes?

Answers

1. the H on the carbonyl carbon atom
2. The carbon-to-oxygen double bond is polar; the carbon-to-carbon double bond is nonpolar.

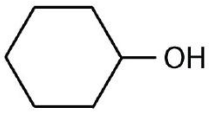
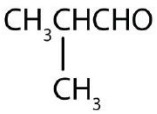
Exercises

1. Which compound in each pair has the higher boiling point?
    1. acetone or 2-propanol
    2. dimethyl ether or acetaldehyde
2. Which compound in each pair has the higher boiling point?
    1. butanal or 1-butanol
    2. acetone or isobutane
3. Draw the structure of the alcohol that could be oxidized to each compound.
    1. cyclohexanone
    2. 2-methyl-1-propanal
4. Draw the structure of the alcohol that could be oxidized to each compound.
    1. 2-pentanone
    2. *o*-methylbenzaldehyde
5. Acetaldehyde is treated with each substance.

1. $Ag^+(aq)$—What inorganic product, if any, is formed?
2. $K_2Cr_2O_7$ in an acid solution—What organic product, if any, is formed?

6. Acetone is treated with each substance.
    1. $Ag^+(aq)$ —What inorganic product, if any, is formed?
    2. $K_2Cr_2O_7$ in an acid solution—What organic product, if any, is formed?

Answers

1. 1. 2-propanol
    2. acetaldehyde
3. 1. 
    2. 

5. 1. silver metal (Ag)
    2. acetic acid (CH_3COOH)

14.11: Organic Sulfur Compounds

Concept Review Exercises

1. What is the functional group of a thiol? Write the condensed structural formula for ethanethiol (ethyl mercaptan).
2. What is the functional group of a disulfide? Write the condensed structural formula for dipropyl disulfide.

Answers

1. SH; CH_3CH_2SH
2. –S–S–; $CH_3CH_2CH_2SSCH_2CH_2CH_3$

Exercises

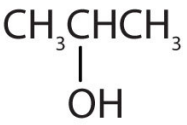
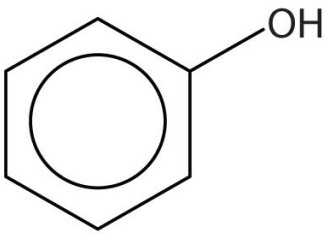
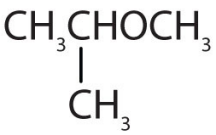
1. A common natural gas odorant is *tert*-butyl mercaptan. What is its condensed structural formula?
2. Write the equation for the oxidation of ethanethiol to diethyl disulfide.

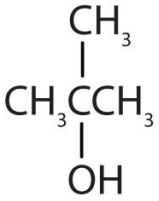
Answer

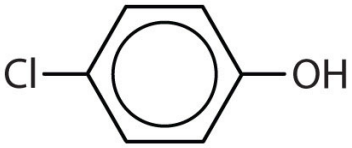
1. $(CH_3)_3CSH$

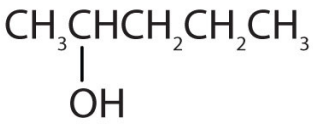
Extra Exercises

1. Describe two ways that ethanol can be prepared. Which method is used to produce alcoholic beverages?
2. Give the structure of the alkene from which isopropyl alcohol is made by reaction with water in an acidic solution.
3. Ethanol is used as a solvent for some drugs that are not soluble in water. Why is methanol not used in medicines?
4. Give the structure of the alkene that is made from *tert*-butyl alcohol [$(CH_3)_3COH$] by reaction with water in an acidic solution.

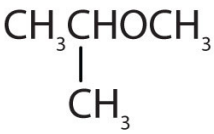
5. Classify each conversion as oxidation, dehydration, or hydration (only the organic starting material and product are shown):
   a. $CH_3OH \rightarrow HCHO$
   b. $CH_3CHOHCH_3 \rightarrow CH_3CH{=}CH_2$
   c. $CH_2{=}CHCH_2CH_3 \rightarrow CH_3CHOHCH_2CH_3$
6. Classify each conversion as oxidation, dehydration, or hydration (only the organic starting material and product are shown.):
   a. $CH_3CHOHCH_3 \rightarrow CH_3COCH_3$
   b. $HOOCCH{=}CHCOOH \rightarrow HOOCCH_2CHOHCOOH$
   c. $2\ CH_3OH \rightarrow CH_3OCH_3$
7. Why is methanol so much more toxic to humans than ethanol?
8. Each of the four isomeric butyl alcohols is treated with potassium dichromate ($K_2Cr_2O_7$) in acid. Give the product (if any) expected from each reaction.
9. Draw the structures and give IUPAC names for the four isomeric aldehydes having the formula $C_5H_{10}O$.
10. Write an equation for the reaction of phenol with aqueous NaOH.
11. Write an equation for the ionization of phenol in water.
12. Draw the structures and give the common and IUPAC names for the three isomeric ketones having the formula $C_5H_{10}O$.
13. As we shall see in Chapter 16 "Carbohydrates", 2,3-dihydroxypropanal and 1,3-dihydroxyacetone are important carbohydrates. Draw their structures.
14. Glutaraldehyde (pentanedial) is a germicide that is replacing formaldehyde as a sterilizing agent. It is less irritating to the eyes, the nose, and skin. Write the condensed structural formula of glutaraldehyde.
15. Why does the oxidation of isopropyl alcohol give a ketone, whereas the oxidation of isobutyl alcohol gives an aldehyde?
16. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary (1°), secondary (2°), or tertiary (3°).
    a. $CH_3CH_2CH_2OH$
    b. 
    c. 
    d. 
17. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary, secondary, or tertiary.
    a. $CH_3CH_2OCH_2CH_3$

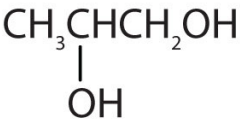
b. 

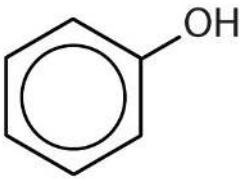
c. 

d. 

18. Tell whether each compound forms an acidic, a basic, or a neutral solution in water.

a. 

b. 

c. 

19. When water is added to ethylene in the presence of an acid catalyst, only one product—ethanol—is possible. However, when water is added to propylene, two products are possible—1-propanol and 2-propanol—but only 2-propanol is formed. In 1870, the Russian chemist Vladimir V. Markovnikov proposed a rule to predict the products of such reactions: Considering water to be HOH, the hydrogen atom of water goes on the carbon atom (of the two involved in the double bond) that has the most hydrogen atoms already bonded to it. The OH group goes on the carbon atom with fewer hydrogen atoms. Use Markovnikov's rule to predict the product of the addition of water to each compound.

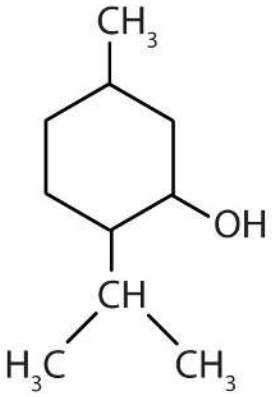
    a. 2-methylpropene
    b. 1-butene
    c. 2-methyl-1-pentene
    d. 2-methyl-2-pentene

20. Ethyl alcohol, like rubbing alcohol (isopropyl alcohol), is often used for sponge baths. What property of alcohols makes them useful for this purpose?

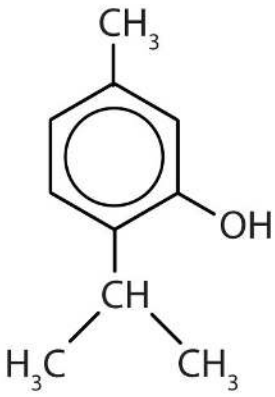
21. In addition to ethanol, the fermentation of grain produces other organic compounds collectively called fusel oils (FO). The four principal FO components are 1-propanol, isobutyl alcohol, 3-methyl-1-butanol, and 2-methyl-1-butanol. Draw a structure for each. (FO is quite toxic and accounts in part for hangovers.)

22. Draw and name the isomeric ethers that have the formula $C_5H_{12}O$.

23. Menthol is an ingredient in mentholated cough drops and nasal sprays. It produces a cooling, refreshing sensation when rubbed on the skin and so is used in shaving lotions and cosmetics. Thymol, the aromatic equivalent of menthol, is the flavoring constituent of thyme.



Menthol



Thymol

a. To what class of compounds does each belong?
b. Give an alternate name for thymol.

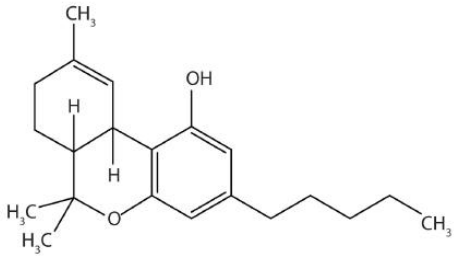
24. Write the equation for the production of ethanol by the addition of water to ethylene. How much ethanol can be made from 14.0 kg of ethylene?

25. Methanol is not particularly toxic to rats. If methanol were newly discovered and tested for toxicity in laboratory animals, what would you conclude about its safety for human consumption?

26. The amino acid cysteine has the formula $HSCH_2CH(NH_2)COOH$. What is the sulfur-containing functional group in the cysteine molecule?

27. The amino acid methionine has the formula $CH_3SCH_2CH_2CH(NH_2)COOH$. What functional groups are in methionine?

28. Tetrahydrocannabinol is the principal active ingredient in marijuana. What functional groups are present in this molecule?



Answers

1. addition of water to ethylene; fermentation (for beverages)

3. Methanol is too toxic.

5.

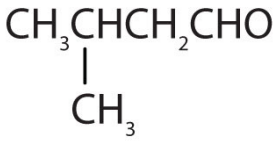
a. oxidation
b. dehydration
c. hydration

7. Methanol is oxidized in the body to toxic formaldehyde; ethanol is oxidized to the less toxic acetaldehyde.

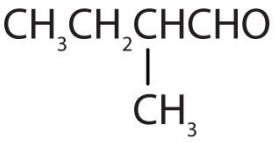
9.



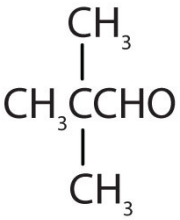
Pentanal



3-Methylbutanal



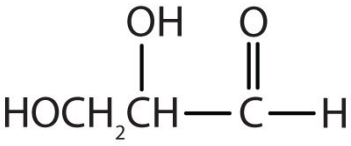
2-Methylbutanal



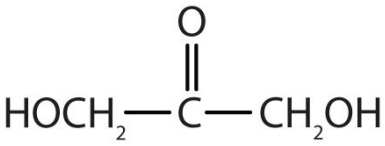
2,2-Dimethylpropanal

11. $C_6H_5OH + H_2O \rightarrow C_6H_5O^- + H_3O^+$

13.



and



15. Isopropyl alcohol is a secondary alcohol, whereas isobutyl alcohol is a primary alcohol.

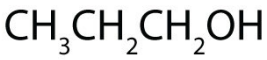
17.

a. ether
b. tertiary alcohol
c. phenol
d. secondary alcohol

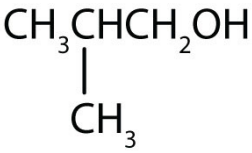
19.

a. *tert*-butyl alcohol
b. 2-butanol
c. 2-methyl-2-pentanol
d. 2-methyl-2-pentanol

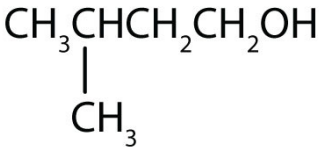
21.



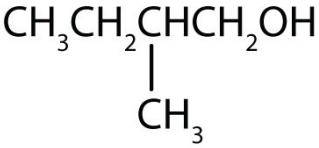
1-Propanol



Isobutyl alcohol



3-Methyl-1-butanol



2-Methyl-1-butanol

23.

a. menthol: alcohol; thymol: phenol
b. 2-isopropyl-5-methylphenol

25. It might be ruled safe until tested on humans.

27. sulfide, amino, and carboxylic acid

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11.S: Organic Compounds of Oxygen (Summary)

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CHAPTER OVERVIEW

12: Carboxylic Acids, Esters, Amines, and Amides

12.1: Prelude to Organic Acids and Bases and Some of Their Derivatives
12.2: Carboxylic Acids - Structures and Names
12.3: The Formation of Carboxylic Acids
12.4: Physical Properties of Carboxylic Acids
12.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization
12.6: Esters - Structures and Names
12.7: Physical Properties of Esters
12.8: Preparation of Esters
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12.14: Physical Properties of Amides
12.15: Formation of Amides
12.16: Chemical Properties of Amides- Hydrolysis
12.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

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12.1: Prelude to Organic Acids and Bases and Some of Their Derivatives

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids.

Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays.

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12.2: Carboxylic Acids - Structures and Names

Learning Objectives

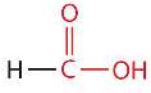
- Name carboxylic acids with common names.
- Name carboxylic acids according to IUPAC nomenclature.

Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure **12.2.1**). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



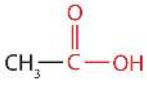
Figure **12.2.1**: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



Formic acid

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Acetic acid

Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often "froze" on the storage shelf. For that reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid (CH_3CH_2COOH), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives. Models of the first four carboxylic acids are shown in Figure **12.2.2**.

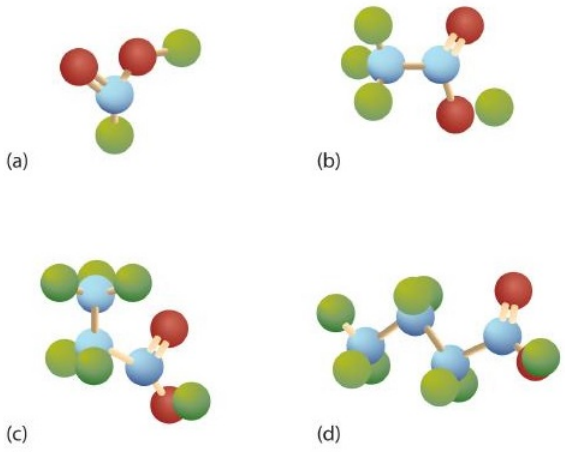
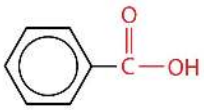


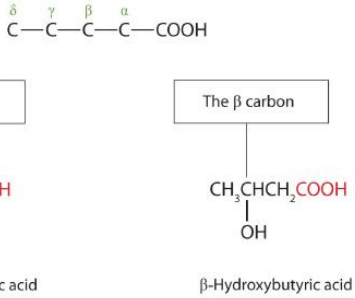
Figure **12.2.2**: Ball-and-Stick Models of Carboxylic Acids. Carboxylic acids feature a carbon atom doubly bonded to an oxygen atom and also joined to an OH group. The four acids illustrated here are formic acid (a), acetic acid (b), propionic acid (c), and butyric acid (d).

The acid with the carboxyl group attached directly to a benzene ring is called benzoic acid (C_6H_5COOH).



Benzoic acid

The common names of carboxylic acids use Greek letters (α, β, γ, δ, and so forth), not numbers, to designate the position of substituent groups in acids. These letters refer to the position of the carbon atom in relation to the carboxyl carbon atom.

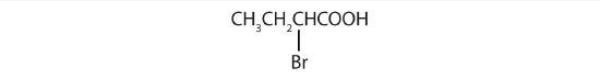


In the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), the parent hydrocarbon is the one that corresponds to the longest continuous chain (LCC) containing the carboxyl group. The *-e* ending of the parent alkane is replaced by the suffix *-oic* and the word *acid*. For example, the carboxylic acid derived from pentane is pentanoic acid ($CH_3CH_2CH_2CH_2COOH$). As with aldehydes, the carboxyl carbon atom is counted first; numbers are used to indicate any substituted carbon atoms in the parent chain.

Greek letters are used with common names; numbers are used with IUPAC names.

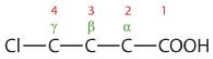
Example 12.2.1

Give the common and IUPAC names for each compound.

1. $ClCH_2CH_2CH_2COOH$
2. 

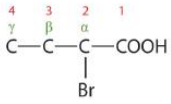
Solution

1. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The chlorine atom is attached to the γ-carbon in the common system or C4 in the IUPAC system. The compound is γ-chlorobutyric acid or 4-chlorobutanoic acid.

2. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The bromine (Br) atom is at the α-carbon in the common system or C2 in the IUPAC system. The compound is α-bromobutyric acid or 2-bromobutanoic acid.

Exercise 12.2.1

Give the IUPAC name for each compound.

a. $ClCH_2CH_2CH_2CH_2COOH$
b. $(CH_3)_2CHCH_2CHBrCOOH$

Example 12.2.2

Write the condensed structural formula for β-chloropropionic acid.

Solution

Propionic acid has three carbon atoms: C–C–COOH. Attach a chlorine (Cl) atom to the parent chain at the beta carbon atom, the second one from the carboxyl group: Cl–C–C–COOH. Then add enough hydrogen atoms to give each carbon atom four bonds: $ClCH_2CH_2COOH$.

Exercise 12.2.2

Write the condensed structural formula for 4-bromo-5-methylhexanoic acid.

Key Takeaways

- Simple carboxylic acids are best known by common names based on Latin and Greek words that describe their source (e.g., formic acid, Latin *formica*, meaning “ant”).
- Greek letters, not numbers, designate the position of substituted acids in the common naming convention.
- IUPAC names are derived from the LCC of the parent hydrocarbon with the *-e* ending of the parent alkane replaced by the suffix *-oic* and the word *acid*.

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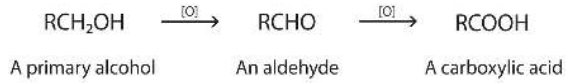
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12.3: The Formation of Carboxylic Acids

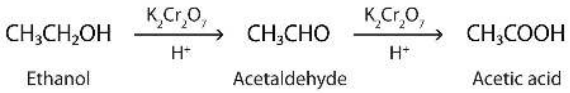
Learning Objectives

- To describe the preparation of carboxylic acids.

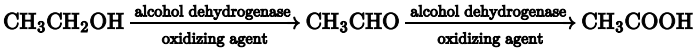
As we noted previously, the oxidation of aldehydes or primary alcohols forms carboxylic acids:



In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.



This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.



Acetic acid can be further oxidized to carbon dioxide and water.

Summary

Whether in the laboratory or in the body, the oxidation of aldehydes or primary alcohols forms carboxylic acids.

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12.4: Physical Properties of Carboxylic Acids

Learning Objectives

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have "goaty" odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure **12.4.1**). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

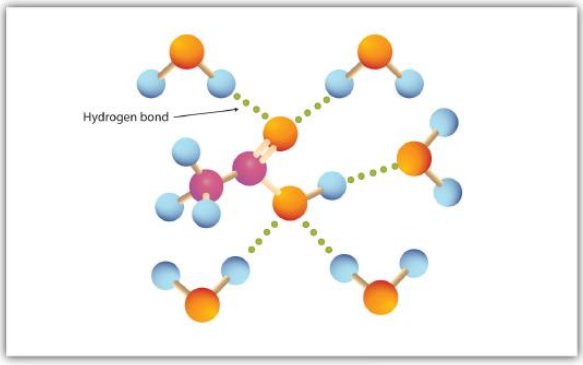


Figure **12.4.1**: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table **12.4.1**: Physical Constants of Carboxylic Acids

Condensed Structural Formula	Name of Acid	Melting Point (°C)	Boiling Point (°C)	Solubility (g/100 g of Water)
HCOOH	formic acid	8	100	miscible
CH_3COOH	acetic acid	17	118	miscible
CH_3CH_2COOH	propionic acid	–22	141	miscible
$CH_3(CH_2)_2COOH$	butyric acid	–5	163	miscible
$CH_3(CH_2)_3COOH$	valeric acid	–35	187	5
$CH_3(CH_2)_4COOH$	caproic acid	–3	205	1.1
C_6H_5COOH	benzoic acid	122	249	0.29

Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

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12.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization

Learning Objectives

- Name the typical reactions that take place with carboxylic acids.
- Describe how carboxylic acids react with basic compounds.

Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions.

$$\mathbf{RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+}$$

Their aqueous solutions exhibit the typical properties of acids, such as changing litmus from blue to red.

The anion formed when a carboxylic acid dissociates is called the *carboxylate* anion ($RCOO^-$).

Whether soluble in water or not, carboxylic acids react with aqueous solutions of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) to form salts:

$$RCOOH + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O$$

$$2RCOOH + Na_2CO_3(aq) \rightarrow 2RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

$$RCOOH + NaHCO_3(aq) \rightarrow RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds. With solutions of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions, they also form carbon dioxide gas.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:

$CH_3COO^-Li^+$	$CH_3CH_2CH_2COO^-K^+$	$C_6H_5COO^-Na^+$
Lithium acetate (lithium ethanoate)	Potassium butyrate (potassium butanoate)	Sodium benzoate

The salts of long-chain carboxylic acids are called soaps. We discuss the chemistry of soaps elsewhere.

$CH_3(CH_2)_{13}CH_2COO^-Na^+$

Sodium palmitate (a soap)

Example 12.5.1

Write an equation for each reaction.

1. the ionization of propionic acid in water (H_2O)
2. the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

Solution

Propionic acid has three carbon atoms, so its formula is CH_2CH_2COOH.

1. Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$
2. Propionic acid reacts with NaOH(aq) to form sodium propionate and water. $CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COO^-Na^+(aq) + H_2O(\ell)$

Exercise 12.5.1

Write an equation for each reaction.

a. the ionization of formic acid in water
b. the ionization of *p*-chlorobenzoic acid in water

Example 12.5.2

Write an equation for the reaction of decanoic acid with each compound.

a. aqueous sodium hydroxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

Solution

a. Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H_2O). $CH_3(CH_2)_8COOH + NaOH(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell)$
b. With $NaHCO_3$, the products are a salt, H_2O, and carbon dioxide (CO_2). $CH_3(CH_2)_8COOH + NaHCO_3(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$

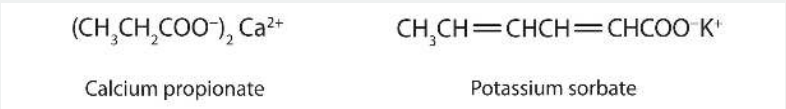
Exercise 12.5.3

Write an equation for the reaction of benzoic acid with each compound.

a. aqueous sodium hydroxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

To Your Health: Organic Salts as Preservatives

Some organic salts are used as preservatives in food products. They prevent spoilage by inhibiting the growth of bacteria and fungi. Calcium and sodium propionate, for example, are added to processed cheese and bakery goods; sodium benzoate is added to cider, jellies, pickles, and syrups; and sodium sorbate and potassium sorbate are added to fruit juices, sauerkraut, soft drinks, and wine. Look for them on ingredient labels the next time you shop for groceries.



Calcium propionate | Potassium sorbate

Key Takeaways

- Soluble carboxylic acids are weak acids in aqueous solutions.
- Carboxylic acids neutralize bases to form salts.

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12.6: Esters - Structures and Names

Learning Objectives

- Identify the general structure for an ester.
- Use common names to name esters.
- Name esters according to the IUPAC system.

Esters have the general formula RCOOR′, where R may be a hydrogen atom, an alkyl group, or an aryl group, and R′ may be an alkyl group or an aryl group but *not* a hydrogen atom. (If it were hydrogen atom, the compound would be a carboxylic acid.) Figure **12.6.1** shows models for two common esters.

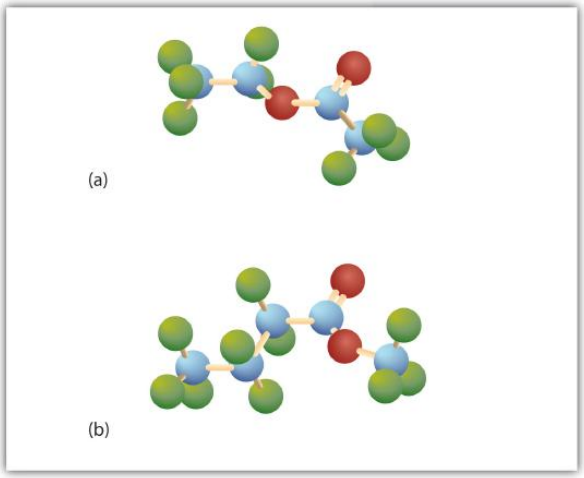


Figure **12.6.1**: The Structure of Esters. Esters feature a carbon-to-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group. The esters shown here are ethyl acetate (a) and methyl butyrate (b).

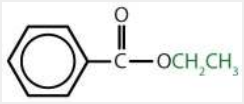
Esters occur widely in nature. Unlike carboxylic acids, esters generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers. Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.

> Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Names of Esters

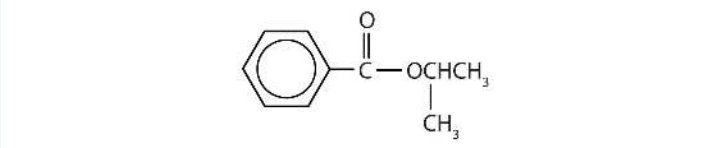
Although esters are covalent compounds and salts are ionic, esters are named in a manner similar to that used for naming salts. The group name of the alkyl or aryl portion is given first and is followed by the name of the acid portion. In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the *-ic* ending of the parent acid is replaced by the suffix *-ate* (Table **12.6.1**).

Table **12.6.1**: Nomenclature of Esters

Condensed Structural Formula	Common Name	IUPAC Name
$HCOOCH_3$	methyl formate	methyl methanoate
CH_3COOCH_3	methyl acetate	methyl ethanoate
$CH_3COOCH_2CH_3$	ethyl acetate	ethyl ethanoate
$CH_3CH_2COOCH_2CH_3$	ethyl propionate	ethyl propanoate
$CH_3CH_2CH_2COOCH(CH_3)_2$	isopropyl butyrate	isopropyl butanoate
	ethyl benzoate	ethyl benzoate

Example 12.6.1

Give the common and IUPAC names for each compound.

1. 
2. 

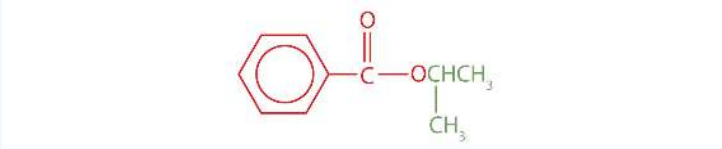
Solution

The alkyl group attached directly to the oxygen atom is a butyl group (in green).



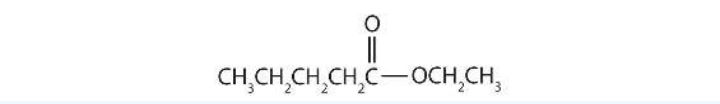
The part of the molecule derived from the carboxylic acid (in red) has three carbon atoms. It is called propionate (common) or propanoate (IUPAC). The ester is therefore butyl propionate or butyl propanoate.

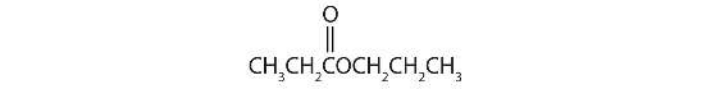
1. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).



Exercise 12.6.1

Give the common and IUPAC names for each compound.

1. 

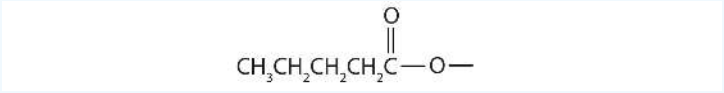


Example 12.6.2

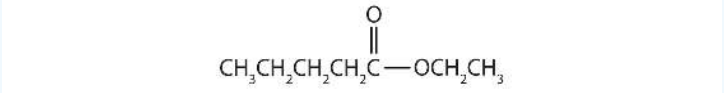
Draw the structure for ethyl pentanoate.

Solution

Start with the portion from the acid. Draw the pentanoate (five carbon atoms) group first; keeping in mind that the last carbon atom is a part of the carboxyl group.



Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



Exercise 12.6.2

Draw the structure for phenyl pentanoate.

Key Takeaway

- An ester has an OR group attached to the carbon atom of a carbonyl group.

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12.7: Physical Properties of Esters

Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table **12.7.1** lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer "dries," leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Table **12.7.1**: *Physical Properties of Some Esters*

Condensed Structural Formula	Name	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Aroma
$HCOOCH_3$	methyl formate	60	−99	32	
$HCOOCH_2CH_3$	ethyl formate	74	−80	54	rum
CH_3COOCH_3	methyl acetate	74	−98	57	
$CH_3COOCH_2CH_3$	ethyl acetate	88	−84	77	
$CH_3CH_2CH_2COOCH_3$	methyl butyrate	102	−85	102	apple
$CH_3CH_2CH_2COOCH_2CH_3$	ethyl butyrate	116	−101	121	pineapple
$CH_3COO(CH_2)_4CH_3$	pentyl acetate	130	−71	148	pear
$CH_3COOCH_2CH_2CH(CH_3)_2$	isopentyl acetate	130	−79	142	banana
$CH_3COOCH_2C_6H_5$	benzyl acetate	150	−51	215	jasmine
$CH_3CH_2CH_2COO(CH_2)_4CH_3$	pentyl butyrate	158	−73	185	apricot
$CH_3COO(CH_2)_7CH_3$	octyl acetate	172	−39	210	orange

Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

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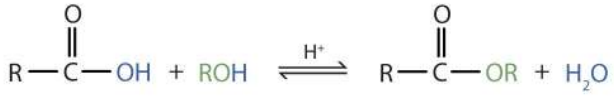
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12.8: Preparation of Esters

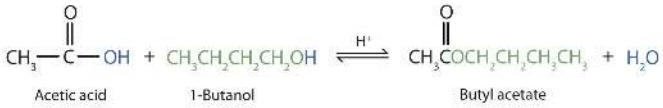
Learning Objectives

- To identify and describe the substances from which most esters are prepared.

Some esters can be prepared by esterification, a reaction in which a carboxylic acid and an alcohol, heated in the presence of a mineral acid catalyst, form an ester and water:



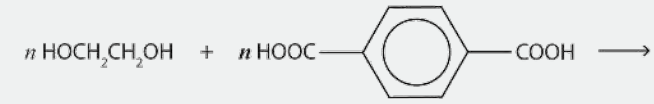
The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.

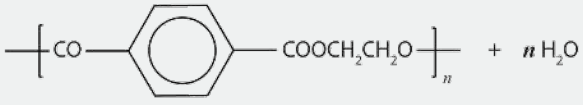


A Closer Look: Condensation Polymers

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:





Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

Summary

Esters are made by the reaction of a carboxylic acid with an alcohol, a process that is called esterification.

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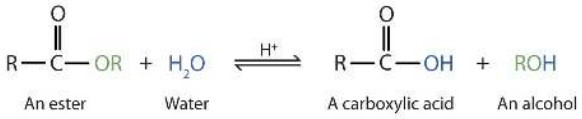
12.9: Hydrolysis of Esters

Learning Objectives

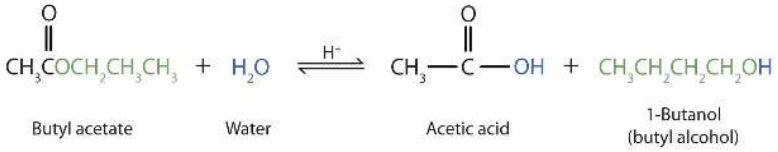
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

Esters are neutral compounds, unlike the acids from which they are formed. In typical reactions, the alkoxy (OR′) group of an ester is replaced by another group. One such reaction is hydrolysis, literally “splitting with water.” The hydrolysis of esters is catalyzed by either an acid or a base.

Acidic hydrolysis is simply the reverse of esterification. The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.



As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.

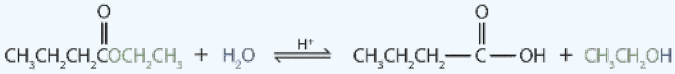


Example 12.9.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($CH_3CH_2CH_2COOCH_2CH_3$) and name the products.

Solution

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:

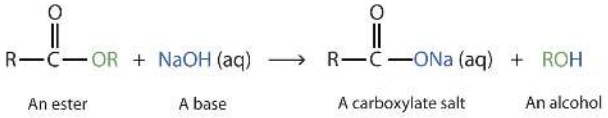


The products are butyric acid (butanoic acid) and ethanol.

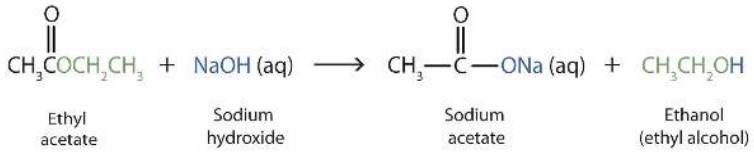
Exercise 12.9.1

Write an equation for the acidic hydrolysis of methyl butanoate and name the products.

When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol. Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning “soap,” and *facere*, meaning “to make”). In a saponification reaction, the base is a reactant, not simply a catalyst. The reaction goes to completion:



As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:

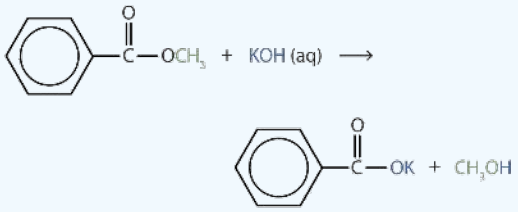


Example 12.9.2

Write an equation for the hydrolysis of methyl benzoate in a potassium hydroxide solution.

Solution

In basic hydrolysis, the molecule of the base splits the ester linkage. The acid portion of the ester ends up as the *salt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.



Exercise 12.9.2

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

Summary

Hydrolysis is a most important reaction of esters. Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Basic hydrolysis of an ester gives a carboxylate salt and an alcohol.

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12.10: Amines - Structures and Names

Learning Objectives

- Identify the general structure for an amine.
- Identify the functional group for amines.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Use nomenclature systems to name amines.

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three (Figure **12.10.1**).

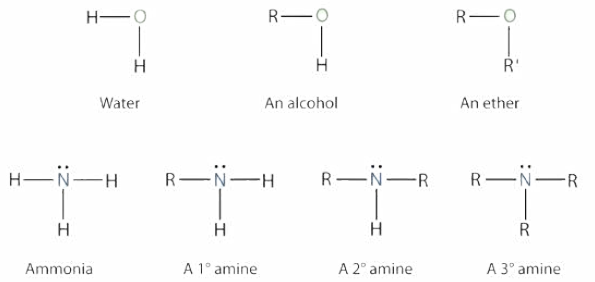


Figure **12.10.1**: The Structure of Amines Compared to Water, an Alcohol, and an Ether

To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.



The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*. (Systematic names are often used by some chemists.) The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups cannot be simply named.

Example 12.10.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

c. $CH_3CH_2NHCH_2CH_3$

d. $CH_3CH_2CH_2NHCH_3$

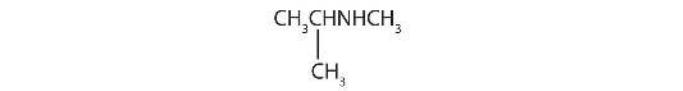
Solution

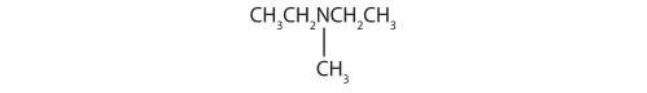
a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.

b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.
d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

Exercise 12.10.1

Name and classify each compound.

a. 

b. 

c. $CH_3CH_2CH_2CH_2NH_2$
d. $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

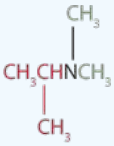
Example 12.10.2

Draw the structure for each compound and classify.

a. isopropyldimethylamine
b. dipropylamine

Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



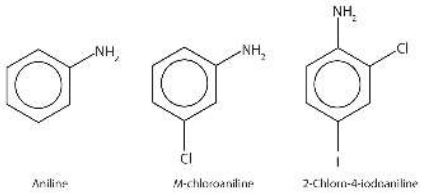
b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

Exercise 12.10.2

Draw the structure for each compound and classify.

a. ethylisopropylamine
b. diethylpropylamine

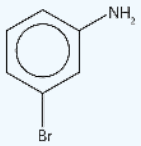
The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.



Aniline *M*-chloroaniline 2-Chlorn-4-iodoaniline

Example 12.10.3

Name this compound.

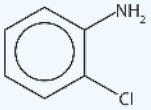


Solution

The benzene ring with an amino (NH_2) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

Exercise 12.10.3

Name this compound.

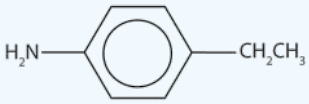


Example 12.10.4

Draw the structure for *p*-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH_2) group.



Exercise 12.10.4

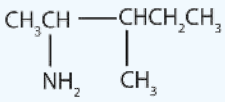
Draw the structure for *p*-isopropylaniline and classify.

Example 12.10.5

Draw the structure for 2-amino-3-methylpentane.

Solution

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.



Exercise 12.10.5

Draw the structure for 2-amino-3-ethyl-1-chloroheptane.

Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion. For example, $CH_3NH_3^+$ is the methylammonium ion. The ion formed from aniline ($C_6H_5NH_3^+$) is called the anilinium ion.

Example 12.10.6

Name each ion.

a. $CH_3NH_3^+$
b. $(CH_3)_2NH_2^+$
c. $(CH_3)_3NH^+$
d. $(CH_3)_4N^+$

Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

a. methylammonium ion
b. dimethylammonium ion
c. trimethylammonium ion
d. tetramethylammonium ion

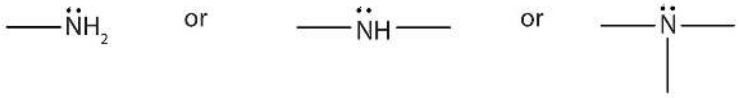
Exercise 12.10.6

Name each ion.

a. $CH_3CH_2NH_3^+$
b. $(CH_3CH_2)_3NH^+$
c. $(CH_3CH_2CH_2)_2NH_2^+$
d. $(CH_3CH_2CH_2CH_2)_4N^+$

Summary

An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The amine functional group is as follows:



Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

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12.11: Physical Properties of Amines

Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure **12.11.1**), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2; −6°C) with those of ethane (CH_3CH_3; −89°C) and methanol (CH_3OH; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table **12.11.1**).

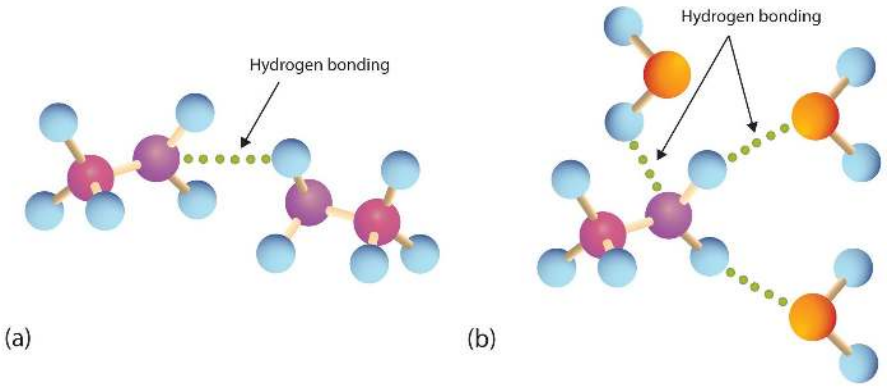


Figure **12.11.1**: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

Table **12.11.1**: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point (°C)	Solubility at 25°C (g/100 g Water)
butylamine	$CH_3CH_2CH_2CH_2NH_2$	1°	73	78	miscible
diethylamine	$(CH_3CH_2)_2NH$	2°	73	55	miscible
butyl alcohol	$CH_3CH_2CH_2CH_2OH$	—	74	118	8
dipropylamine	$(CH_3CH_2CH_2)_2NH$	2°	101	111	4
triethylamine	$(CH_3CH_2)_3N$	3°	101	90	14
dipropyl ether	$(CH_3CH_2CH_2)_2O$	—	102	91	0.25

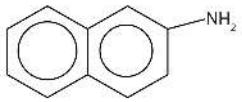
All three classes of amines can engage in hydrogen bonding with water (Figure **12.11.1***b*). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.

$$HOCH_2CH_2OH$$

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Key Takeaways

- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

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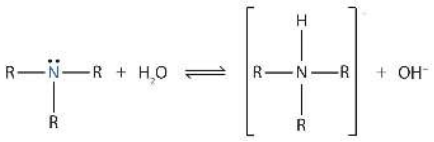
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12.12: Amines as Bases

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 12.12.1

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 12.12.1

What are the formulas of the acid and base that react to form $\mathbf{(CH_3CH_2CH_2)_3NH^+I^-}$?

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

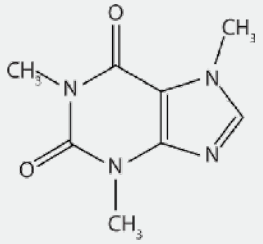
Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning “other”), nitrogen, oxygen, sulfur, or some other atom is incorporated 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.

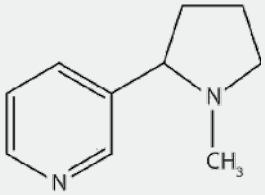
To Your Health: Three Well-Known Alkaloids

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.



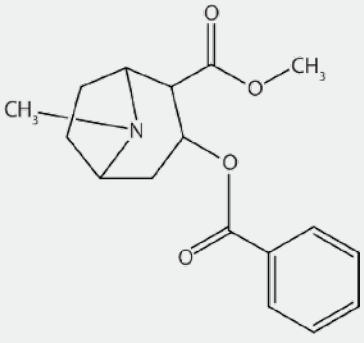
Caffeine

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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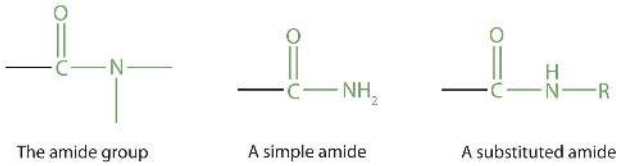
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12.13: Amides- Structures and Names

Learning Objectives

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Names amides with common names.
- Name amides according to the IUPAC system.

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



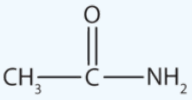
The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

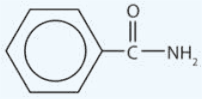
Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



Example 12.13.1

Name each compound with the common name, the IUPAC name, or both.

a. 

b. 

Solution

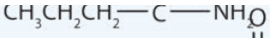
a. This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an NH_2 group. The *-ic* from *acetic* (or *-oic* from ethanoic) is dropped, and *-amide* is added to give *acetamide* (or ethanamide in the IUPAC system).

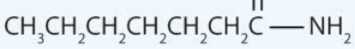
b. This amide is derived from benzoic acid. The *-oic* is dropped, and *-amide* is added to give benzamide.

Exercise 12.13.1

Name each compound with the common name, the IUPAC name, or both.

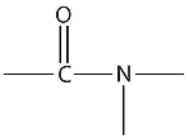


a. 

b. 

Key Takeaways

- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.
- The functional group for an amide is as follows:



- In names for amides, the *-ic acid* of the common name or the *-oic* ending of the IUPAC for the corresponding carboxylic acid is replaced by *-amide*.

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12.14: Physical Properties of Amides

Learning Objectives

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

With the exception of formamide ($HCONH_2$), which is a liquid, all simple amides are solids (Table **12.14.1**). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table **12.14.1**: *Physical Constants of Some Unsubstituted Amides*

Condensed Structural Formula	Name	Melting Point (°C)	Boiling Point (°C)	Solubility in Water
$HCONH_2$	formamide	2	193	soluble
CH_3CONH_2	acetamide	82	222	soluble
$CH_3CH_2CONH_2$	propionamide	81	213	soluble
$CH_3CH_2CH_2CONH_2$	butyramide	115	216	soluble
$C_6H_5CONH_2$	benzamide	132	290	slightly soluble

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure **12.14.1**). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

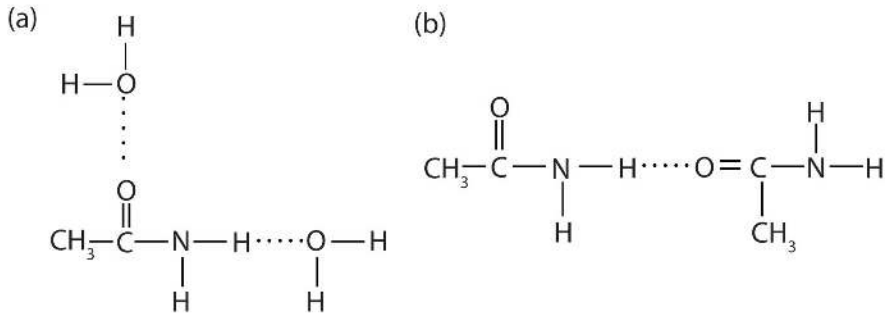


Figure **12.14.1**: Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

Key Takeaways

- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of five or fewer carbon atoms are soluble in water?.

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12.15: Formation of Amides

Learning Objectives

- To describe the preparation procedure for amides.

The addition of ammonia (NH_3) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

Polyamides

Just as the reaction of a diol and a diacid forms a polyester, the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.

$$\underset{\text{1,6-Hexanediamine}}{n\,H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2} + \underset{\text{Adipic acid}}{n\,HOOCCH_2CH_2CH_2CH_2COOH} \longrightarrow$$

$$\underset{\text{Nylon 66 (a polyamide)}}{-\!\!-HN[COCH_2CH_2CH_2CH_2CONHCH_2CH_2CH_2CH_2CH_2CH_2NH]_nCO-\!\!-} + 2n\,H_2O$$

Some polyamides are known as *nylons*. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

Key Takeaway

- Amides are prepared by the reaction of a carboxylic acid with ammonia or an amine.

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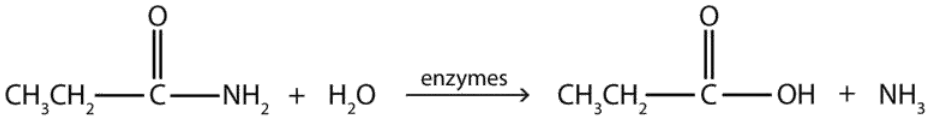
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12.16: Chemical Properties of Amides- Hydrolysis

Learning Objectives

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:



> *Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.*

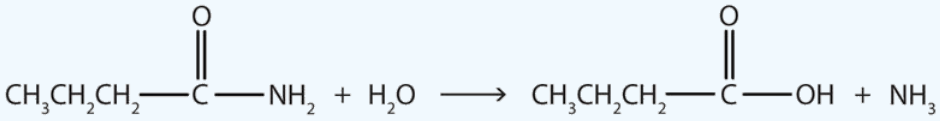
Example 12.16.1

Write the equation for the hydrolysis of each compound.

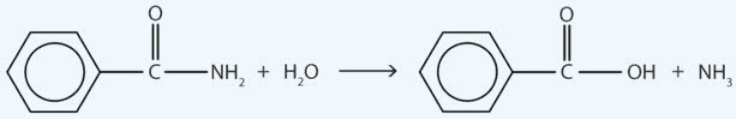
a. butyramide
b. benzamide

Solution

a. The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric acid and ammonia.



- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.



Exercise 12.16.1

Write the equation for the hydrolysis of each compound.

a. propionamide (propanamide)
b. hexanamide

Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology,

chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

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12.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.

A **carboxylic acid** (RCOOH) contains the functional group COOH, called the **carboxyl group**, which has an OH group attached to a carbonyl carbon atom. An **ester** (RCOOR′) has an OR′ group attached to a carbonyl carbon atom. An **amine** is derived from ammonia (NH_3), with one, two, or all three of the hydrogen atoms of NH_3 replaced by an alkyl (or an aryl) group. The **amide** functional group has a carbonyl group joined to a nitrogen atom from NH_3 or an amine.

There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, CH_2COOH), or an aryl group (as in benzoic acid, C_6H_5COOH). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry).

A carboxylic acid is formed by the oxidation of an aldehyde with the same number of carbon atoms. Because aldehydes are formed from primary alcohols, these alcohols are also a starting material for carboxylic acids.

Carboxylic acids have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

Carboxylic acids are weak acids. They react with bases to form salts and with carbonates and bicarbonates to form carbon dioxide gas and the salt of the acid.

Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Esters can be synthesized by **esterification**, in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

Inorganic acids also react with alcohols to form esters. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Amines are nitrogen-containing organic molecules derived from ammonia (NH_3). A **primary (1°) amine** (RNH_2) has one organic group bonded to the nitrogen atom, a **secondary (2°) amine** (R_2NH) has two organic groups bonded to the nitrogen atom, and a **tertiary (3°) amine** (R_3N) has three organic groups bonded to the nitrogen atom. Amines are basic compounds that react with strong acids to produce ammonium (NH_4^+) salts. A cyclic compound in which the ring contains one or more noncarbon atoms is called a **heterocyclic compound**. There are many heterocyclic amines, including many physiologically important ones. **Alkaloids** are heterocyclic amines found in many plants. Caffeine, nicotine, and cocaine are familiar alkaloids.

Organic compounds containing a carbonyl group bonded to a nitrogen atom are amides, and the carbon-to-nitrogen bond is an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. Amides are synthesized from carboxylic acids and NH_3 or amines. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

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CHAPTER OVERVIEW

13: Carbohydrates

13.1: Prelude to Carbohydrates
13.2: Carbohydrates
13.3: Classes of Monosaccharides
13.4: Important Hexoses
13.5: Cyclic Structures of Monosaccharides
13.6: Properties of Monosaccharides
13.7: Disaccharides
13.8: Polysaccharides
13.S: Carbohydrates (Summary)

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13.1: Prelude to Carbohydrates

In the United States, 17.9 million people have been diagnosed with diabetes, and experts estimate that at least another 5.7 million people have the disease but have not been diagnosed. In 2006, diabetes was the seventh leading cause of death, listed on 72,507 death certificates. Moreover, it was a contributing factor in over 200,000 deaths in which the cause was listed as something else, such as heart or kidney disease.

People with diabetes are impaired in their ability to metabolize glucose, a sugar needed by the body for energy; as a result, excessive quantities of glucose accumulate in the blood and the urine. The characteristic symptoms of diabetes are weight loss, constant hunger, extreme thirst, and frequent urination (the kidneys excrete large amounts of water in an attempt to remove the excess sugar from the blood).

An important diagnostic test for diabetes is the oral glucose tolerance test, which measures the level of glucose in blood plasma. A first measurement is made after a fast of at least 8 h, followed by another measurement 2 h after the person drinks a flavored solution of 75 g of glucose dissolved in water. At the second measurement, the glucose plasma level should be no higher than 139 mg/dL. Individuals with a value between 140 and 199 mg/dL are diagnosed with prediabetes, while those with a value of 200 mg/dL or above are diagnosed with diabetes. Following a diagnosis of diabetes a person will need to monitor his or her blood glucose levels daily (or more often) using a glucose meter.



Figure **13.1.1**: Using a Glucose Meter to Test Blood Glucose Level. (Public Domain; Centers for Disease Control and Prevention).

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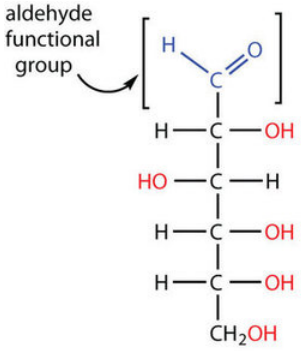
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13.2: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

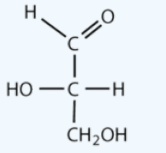
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. 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 $C_6{\cdot}6H_2O$.

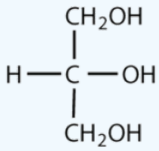


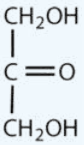
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

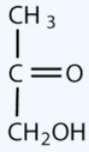
Example 13.2.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.

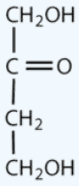
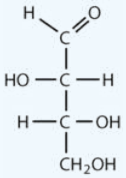
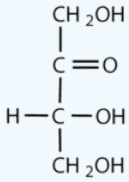
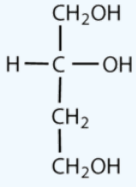
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

? Exercise 13.2.1

Which compounds would be classified as carbohydrates?

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:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{13.2.1}$$

(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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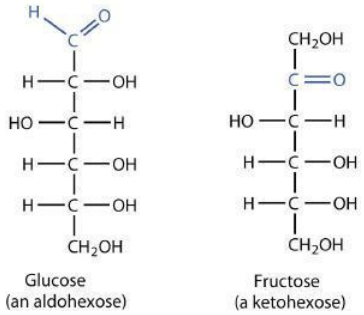
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13.3: Classes of Monosaccharides

Learning Objectives

- Classify monosaccharides as aldoses or ketoses and as trioses, tetroses, pentoses, or hexoses.
- Distinguish between a D sugar and an L sugar.

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.



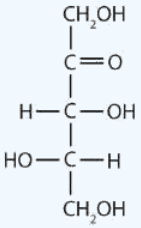
Example 13.3.1

Draw an example of each type of compound.

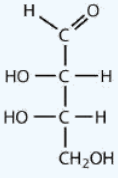
a. a ketopentose
b. an aldotetrose

Solution

a. The structure must have five carbon atoms with the second carbon atom being a carbonyl group and the other four carbon atoms each having an OH group attached. Several structures are possible, but one example is shown.



- The structure must have four carbon atoms with the first carbon atom part of the aldehyde functional group. The other three carbon atoms each have an OH group attached. Several structures are possible, but one example is shown.



? Exercise 13.3.1

Draw an example of each type of compound.

a. an aldohexose
b. a ketotetrose

The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure **13.3.1**; glyceraldehyde is an aldotriose, while dihydroxyacetone is a ketotriose. Notice that two structures are shown for glyceraldehyde. These structures are stereoisomers, and hence are isomers having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space. If you make models of the two stereoisomers of glyceraldehyde, you will find that you cannot place one model on top of the other and have each functional group point in the same direction. However, if you place one of the models in front of a mirror, the image in the mirror will be identical to the second stereoisomer in part (b) of Figure **13.3.1**. Molecules that are nonsuperimposable (nonidentical) mirror images of each other are a type of stereoisomer called enantiomers (Greek *enantios*, meaning "opposite").

Note

These are another type of stereoisomers than the *cis-trans* (geometric) isomers previously discussed.

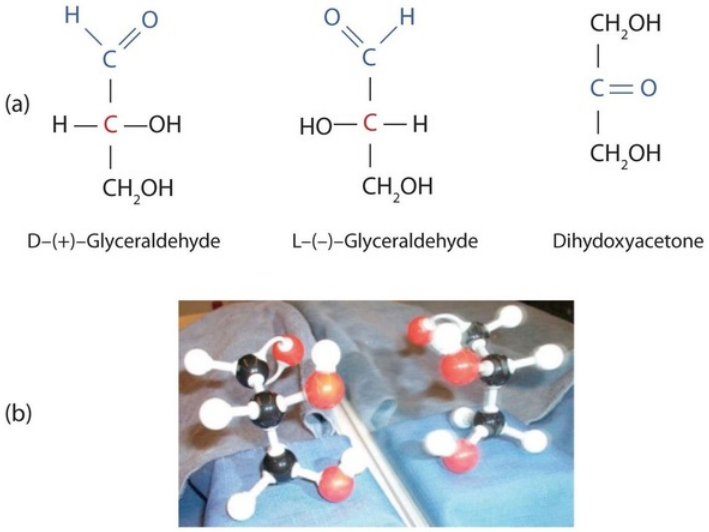


Figure **13.3.1**: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

A key characteristic of enantiomers is that they have a carbon atom to which four different groups are attached. Note, for example, the four different groups attached to the central carbon atom of glyceraldehyde (part (a) of Figure **13.3.1**). A carbon atom that has four different groups attached is a chiral carbon. If a molecule contains one or more chiral carbons, it is likely to exist as two or more stereoisomers. Dihydroxyacetone does not contain a chiral carbon and thus does not exist as a pair of stereoisomers. Glyceraldehyde, however, has a chiral carbon and exists as a pair of enantiomers. Except for the direction in which each enantiomer rotates plane-polarized light, these two molecules have identical physical properties. One enantiomer has a specific rotation of +8.7°, while the other has a specific rotation of −8.7°.

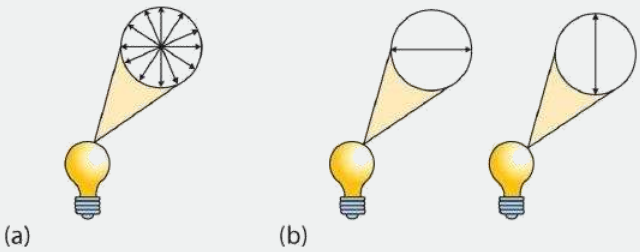
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure **13.3.1**. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that are attached to each chiral carbon are written to the right or left. (If the monosaccharide is a ketose, the ketone functional group is the second carbon atom.) Vertical lines represent bonds pointing away from you, while horizontal lines represent bonds coming toward you. The formulas of chiral molecules represented in this manner are referred to as **Fischer projections**.

The two enantiomers of glyceraldehyde are especially important because monosaccharides with more than three carbon atoms can be considered as being derived from them. Thus, D- and L-glyceraldehyde provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections terminate in the same configuration as D-glyceraldehyde are designated as D sugars; those derived from L-glyceraldehyde are designated as L sugars.

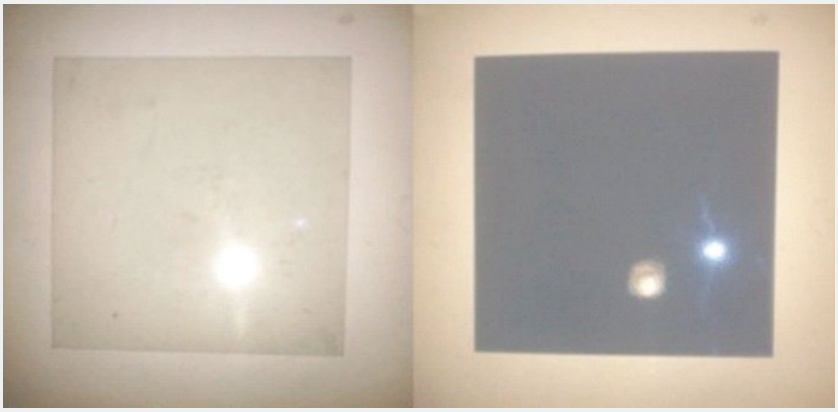
> *By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.*

Looking Closer: Polarized Light

A beam of ordinary light can be pictured as a bundle of waves; some move up and down, some sideways, and others at all other conceivable angles. When a beam of light has been polarized, however, the waves in the bundle all vibrate in a single plane. Light altered in this way is called *plane-polarized light*. Much of what chemists know about stereoisomers comes from studying the effects they have on plane-polarized light. In this illustration, the light on the left is not polarized, while that on the right is polarized.



Sunlight, in general, is not polarized; light from an ordinary light bulb or an ordinary flashlight is not polarized. One way to polarize ordinary light is to pass it through Polaroid sheets, special plastic sheets containing carefully oriented organic compounds that permit only light vibrating in a single plane to pass through. To the eye, polarized light doesn't "look" any different from nonpolarized light. We can detect polarized light, however, by using a second sheet of polarizing material, as shown here.



In the photo on the left, two Polaroid sheets are aligned in the same direction; plane-polarized light from the first Polaroid sheet can pass through the second sheet. In the photo on the right, the top Polaroid sheet has been rotated 90° and now blocks the plane-polarized light that comes through the first Polaroid sheet.

Certain substances act on polarized light by rotating the plane of vibration. Such substances are said to be optically active. The extent of optical activity is measured by a polarimeter, an instrument that contains two polarizing lenses separated by a sample tube, as shown in the accompanying figure. With the sample tube empty, maximum light reaches the observer's eye when the two lenses are aligned so that both pass light vibrating in the same plane. When an optically active substance is placed in the sample tube, that substance rotates the plane of polarization of the light passing through it, so that the polarized light emerging from the

sample tube is vibrating in a different direction than when it entered the tube. To see the maximum amount of light when the sample is in place, the observer must rotate one lens to accommodate the change in the plane of polarization.

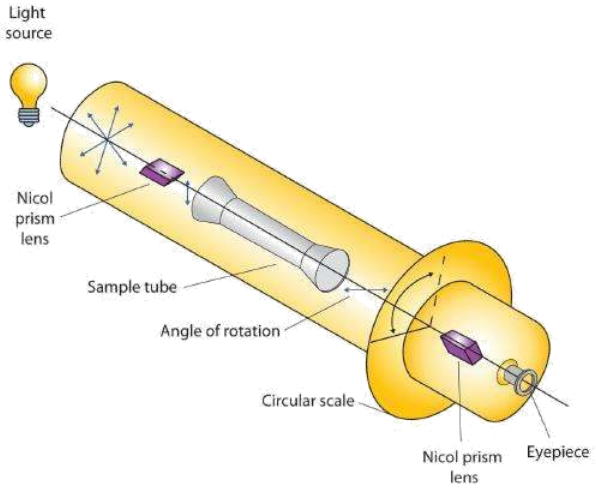


Figure **13.3.2**: Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light to the right (clockwise) from the observer's point of view. These compounds are said to be dextrorotatory; substances that rotate light to the left (counterclockwise) are levorotatory. To denote the direction of rotation, a positive sign (+) is given to dextrorotatory substances, and a negative sign (−) is given to levorotatory substances.

Summary

Monosaccharides can be classified by the number of carbon atoms in the structure and/or the type of carbonyl group they contain (aldose or ketose). Most monosaccharides contain at least one chiral carbon and can form stereoisomers. Enantiomers are a specific type of stereoisomers that are mirror images of each other.

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13.4: Important Hexoses

Learning Objectives

- To identify the structures of D-glucose, D-galactose, and D-fructose and describe how they differ from each other.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **13.4.1**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

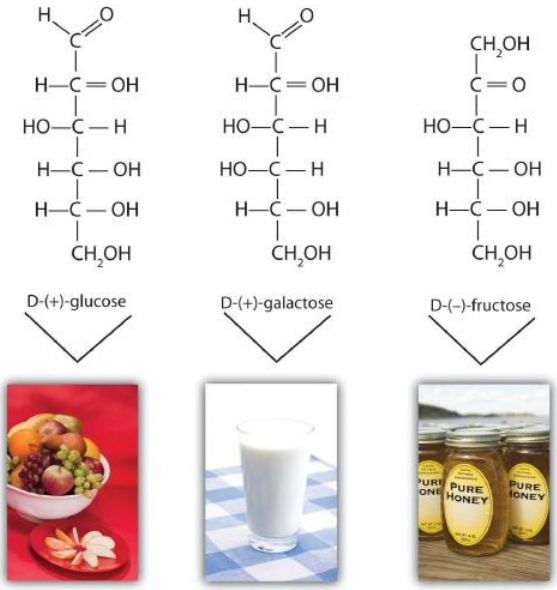


Figure **13.4.1**: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

Glucose

D-Glucose, generally referred to as simply glucose, is the most abundant sugar found in nature; most of the carbohydrates we eat are eventually converted to it in a series of biochemical reactions that produce energy for our cells. It is also known by three other names: *dextrose*, from the fact that it rotates plane-polarized light in a clockwise (dextrorotatory) direction; *corn sugar* because in the United States cornstarch is used in the commercial process that produces glucose from the hydrolysis of starch; and *blood sugar* because it is the carbohydrate found in the circulatory system of animals. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

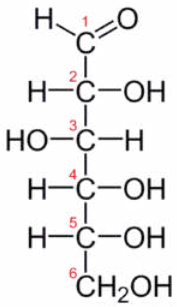


Figure **13.4.2**: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure **13.4.2**. Glucose is a D sugar because the OH group on the fifth carbon atom (the chiral center farthest from the carbonyl group) is on the right. In fact, all the OH groups except the one on the third carbon atom are to the right.

Galactose

D-Galactose does not occur in nature in the uncombined state. It is released when lactose, a disaccharide found in milk, is hydrolyzed. The galactose needed by the human body for the synthesis of lactose is obtained by the metabolic conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*. The structure of D-galactose is shown in Figure **13.4.1**. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure **13.4.1**, is the most abundant ketohexose. Note that from the third through the sixth carbon atoms, its structure is the same as that of glucose. It occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. Fructose (from the Latin *fructus*, meaning "fruit") is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (Table **13.4.1**).

Table **13.4.1**: The Relative Sweetness of Some Compounds (Sucrose = 100)

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

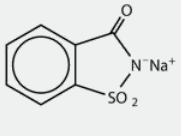
Looking Closer: Artificial Sweeteners

Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

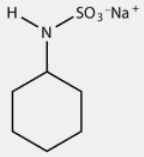
The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the

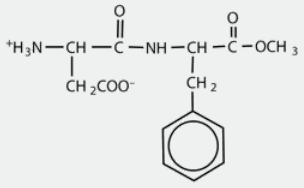
FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



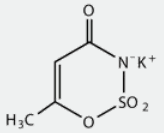
Saccharin



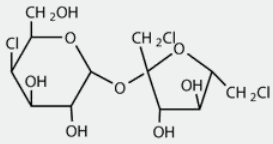
Cyclamate



Aspartame



Acesulfame K



Sucralose

A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

Summary

Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.

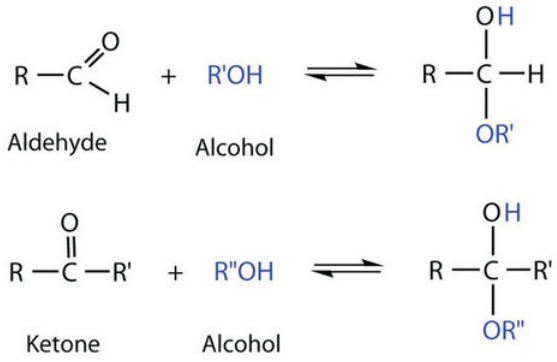
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13.5: Cyclic Structures of Monosaccharides

Learning Objectives

- Define what is meant by anomers and describe how they are formed.
- Explain what is meant by mutarotation.

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. This conversion occurs because of the ability of aldehydes and ketones to react with alcohols:



You might wonder why the aldehyde reacts with the OH group on the fifth carbon atom rather than the OH group on the second carbon atom next to it. Recall that cyclic alkanes containing five or six carbon atoms in the ring are the most stable. The same is true for monosaccharides that form cyclic structures: rings consisting of five or six carbon atoms are the most stable.

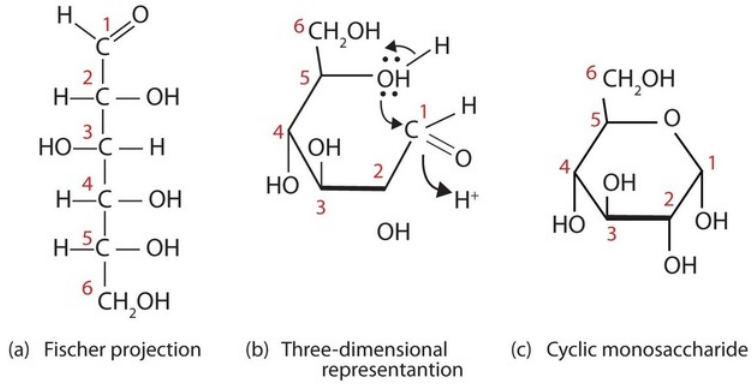


Figure 13.5.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide, such as any of the structures shown in Figure 13.5.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 13.5.2. The structure shown on the left side of Figure 13.5.2, with the OH group on the first carbon atom projected downward, represent what is called the *alpha (α) form*. The structures on the right side, with the OH group on the first carbon atom pointed upward, is the *beta (β) form*. These two stereoisomers of a cyclic monosaccharide are known as anomers; they differ in structure around the anomeric carbon—that is, the carbon atom that was the carbonyl carbon atom in the straight-chain form.

It is possible to obtain a sample of crystalline glucose in which all the molecules have the α structure or all have the β structure. The α form melts at 146°C and has a specific rotation of +112°, while the β form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium (part (a) of Figure 13.5.2). You can start with a pure crystalline sample of glucose consisting entirely of either anomer, but as soon as the molecules dissolve in water, they open to form the carbonyl group and then reclose to form either the α or the β anomer. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as mutarotation (Latin *mutare*, meaning “to change”). At equilibrium, the mixture consists of

about 36% α-D-glucose, 64% β-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°.

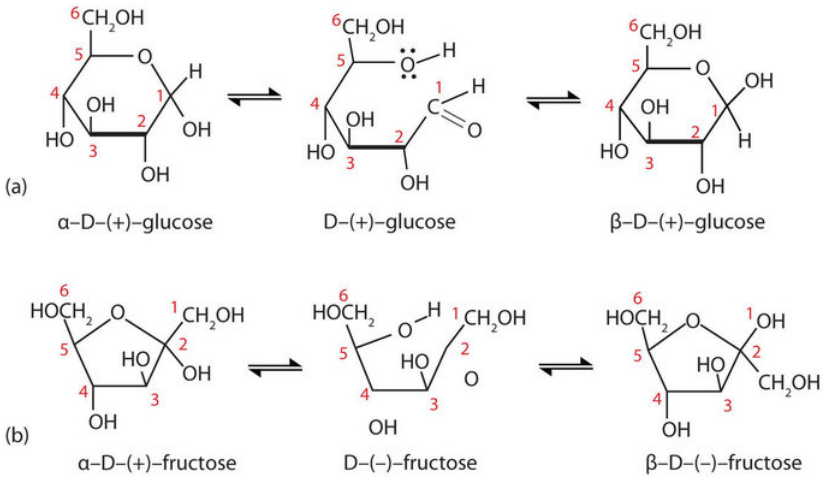


Figure **13.5.2**: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Even though only a small percentage of the molecules are in the open-chain aldehyde form at any time, the solution will nevertheless exhibit the characteristic reactions of an aldehyde. As the small amount of free aldehyde is used up in a reaction, there is a shift in the equilibrium to yield more aldehyde. Thus, *all* the molecules may eventually react, even though very little free aldehyde is present at a time.

Commonly, (e.g., in Figures **13.5.1** and **13.5.2**) the cyclic forms of sugars are depicted using a convention first suggested by Walter N. Haworth, an English chemist. The molecules are drawn as planar hexagons with a darkened edge representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the right in a Fischer projection appears below the plane of the ring in a Haworth projection, and any group written to the left in a Fischer projection appears above the plane in a Haworth projection.

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together.

Summary

Monosaccharides that contain five or more carbons atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. In an aqueous solution, an equilibrium mixture forms between the two anomers and the straight-chain structure of a monosaccharide in a process known as mutarotation.

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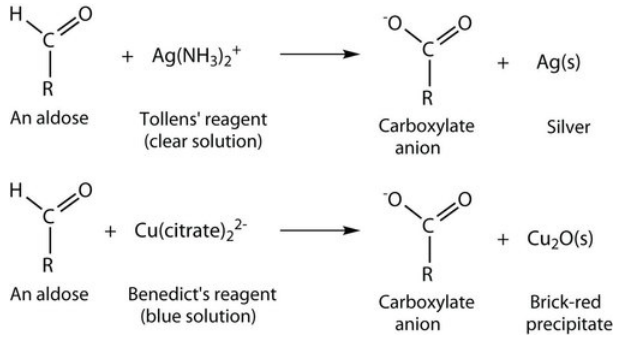
13.6: Properties of Monosaccharides

Learning Objectives

- To identify the physical and chemical properties of monosaccharides.

Monosaccharides such as glucose and fructose are crystalline solids at room temperature, but they are quite soluble in water, each molecule having several OH groups that readily engage in hydrogen bonding. The chemical behavior of these monosaccharides is likewise determined by their functional groups.

An important reaction of monosaccharides is the oxidation of the aldehyde group, one of the most easily oxidized organic functional groups. Aldehyde oxidation can be accomplished with any mild oxidizing agent, such as Tollens' reagent or Benedict's reagent. With the latter, complexed copper(II) ions are reduced to copper(I) ions that form a brick-red precipitate [copper(I) oxide; Figure **13.6.1**].



Any carbohydrate capable of reducing either Tollens' or Benedict's reagents without first undergoing hydrolysis is said to be a reducing sugar. Because both the Tollens' and Benedict's reagents are basic solutions, ketoses (such as fructose) also give positive tests due to an equilibrium that exists between ketoses and aldoses in a reaction known as *tautomerism*.

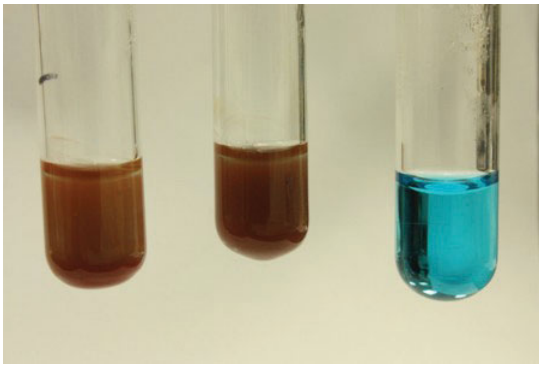


Figure **13.6.1**: Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.

These reactions have been used as simple and rapid diagnostic tests for the presence of glucose in blood or urine. For example, Clinitest tablets, which are used to test for sugar in the urine, contain copper(II) ions and are based on Benedict's test. A green color indicates very little sugar, whereas a brick-red color indicates sugar in excess of 2 g/100 mL of urine.

Summary

Monosaccharides are crystalline solids at room temperature and quite soluble in water. Monosaccharides are reducing sugars; they reduce mild oxidizing agents, such as Tollens' or Benedict's reagents.

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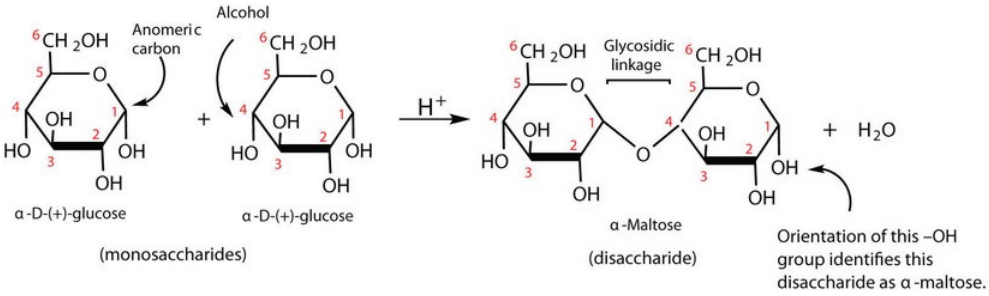
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13.7: Disaccharides

Learning Objectives

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol. Disaccharides ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a glycosidic linkage. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide.



The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll consider each sugar in more detail.

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.

$$\text{maltose} \xrightarrow{\text{H}^+ \text{ or maltase}} 2\ \text{D-glucose}$$

Maltose is a reducing sugar. Thus, its two glucose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic linkage; see Figure **13.7.1**). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucose can be in either the α or the β position, as shown in Figure **13.7.1**.

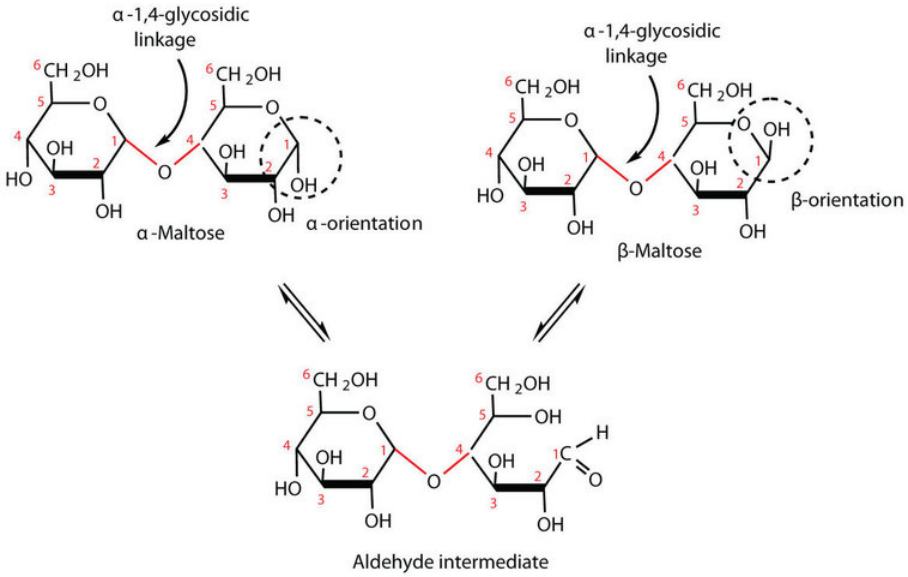
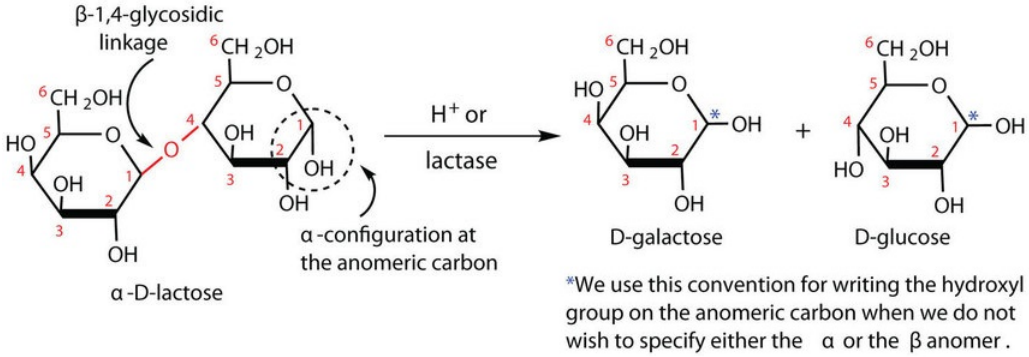


Figure **13.7.1**: An Equilibrium Mixture of Maltose Isomers

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

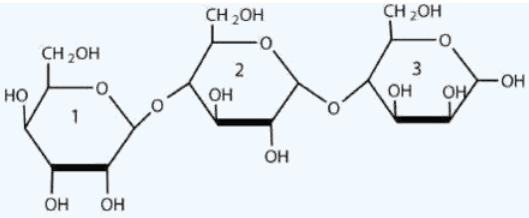
Lactose is a reducing sugar composed of one molecule of D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*:



Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

Example 13.7.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.

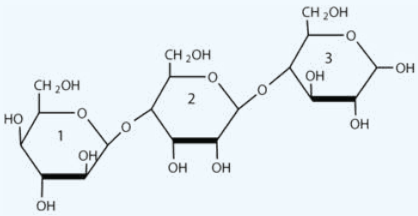


Solution

The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

? Exercise 13.7.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.



To Your Health: Lactose Intolerance and Galactosemia

Lactose makes up about 40% of an infant's diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world's adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people the inability to synthesize sufficient enzyme increases with age. Up to 20% of the US population suffers some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

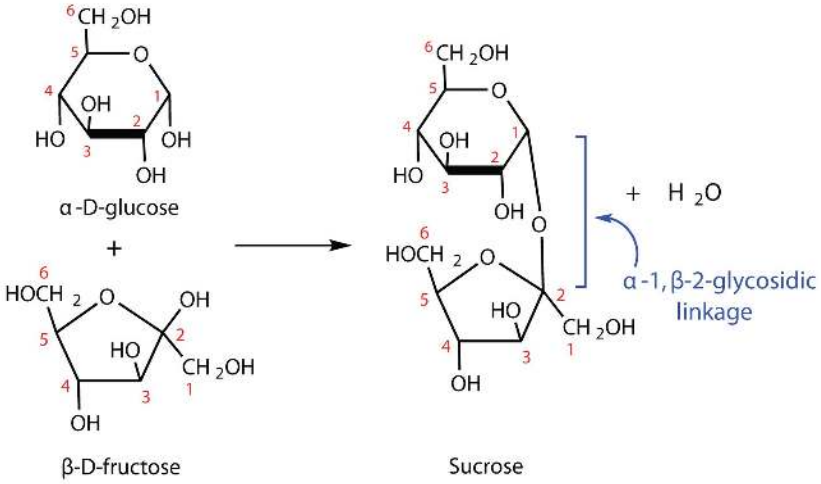
The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α-1,β-2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α-D-glucose and the OH group on the anomeric carbon of β-D-fructose, it ties up the anomeric carbons of both glucose and fructose.



This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide "uncyclizes" to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body's requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

Summary

Maltose is composed of two molecules of glucose joined by an α-1,4-glycosidic linkage. It is a reducing sugar that is found in sprouting grain. Lactose is composed of a molecule of galactose joined to a molecule of glucose by a β-1,4-glycosidic linkage. It is a reducing sugar that is found in milk. Sucrose is composed of a molecule of glucose joined to a molecule of fructose by an α-1,β-2-glycosidic linkage. It is a nonreducing sugar that is found in sugar cane and sugar beets

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13.8: Polysaccharides

Learning Objectives

- To compare and contrast the structures and uses of starch, glycogen, and cellulose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a “starchy” food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure **13.8.1**). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure **13.8.1**). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

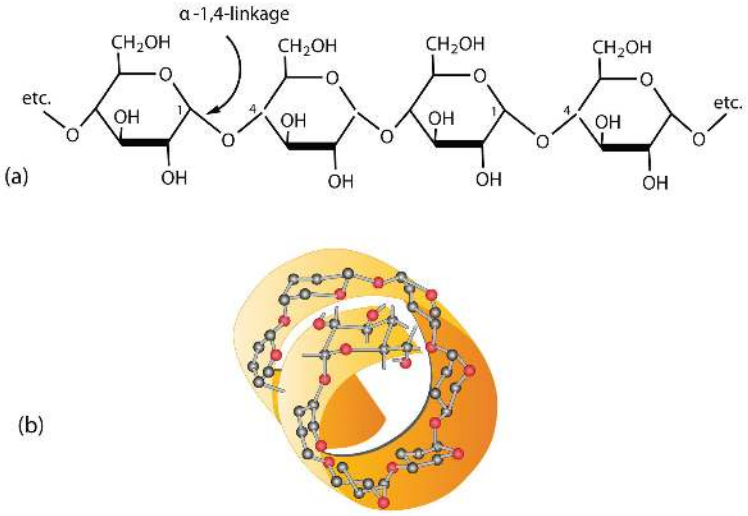


Figure **13.8.1**: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure **13.8.2**). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

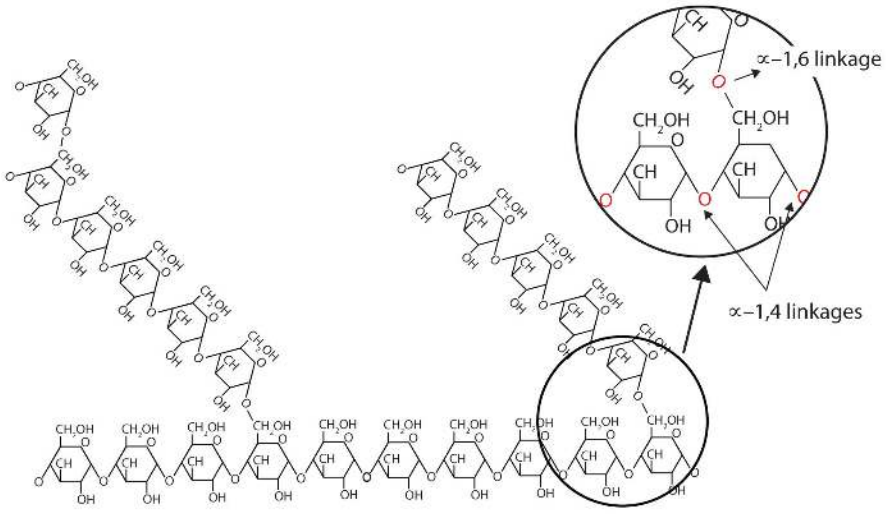


Figure **13.8.2**: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> *About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.*

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure **13.8.3**). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure **13.8.3**). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

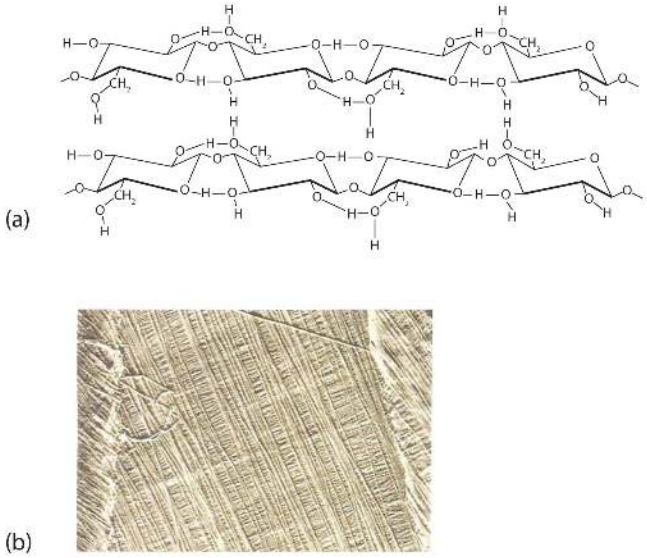


Figure **13.8.3**: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

> Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Summary

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin. Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

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13.S: Carbohydrates (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Those with two monosaccharide units are **disaccharides**, and those with many monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the *alpha* form is drawn with the OH group on the "former" carbonyl carbon atom (**anomeric carbon**) pointing downward; the *beta* form, with the OH group pointing upward; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

The carbonyl group present in monosaccharides is easily oxidized by Tollens' or Benedict's reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide *sucrose* (table sugar) consists of a glucose unit and a fructose unit joined by a glycosidic linkage. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body's energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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CHAPTER OVERVIEW

14: Lipids

14.1: Prelude to Lipids
14.2: Fatty Acids
14.3: Fats and Oils
14.4: Membranes and Membrane Lipids
14.5: Steroids
14.S: Lipids (Summary)

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14.1: Prelude to 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 **14.1.1** 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.

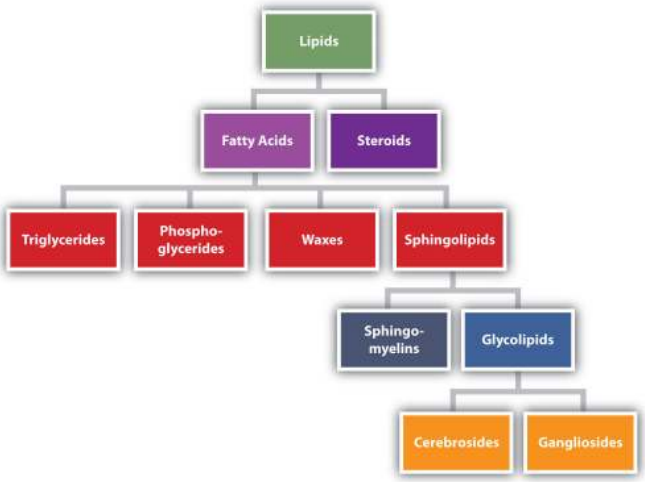


Figure **14.1.1**: Lipid Organization Based on Structural Relationships

Lipid categorized into fatty acids and steroids. Fatty acids are further separated into triglycerides, phospho-glycerides, waxes, and sphingolipids. Sphingolipids are separated into sphingo-myelins and glycolipids. Glycolipids are separated into cerebrosides and gangliosides.

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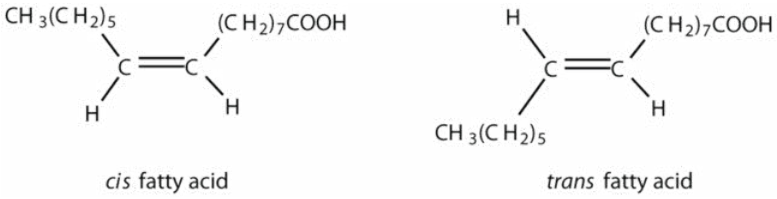
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14.2: Fatty Acids

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table **14.2.1** 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 **14.2.1**: Some Common Fatty Acids Found in Natural Fats

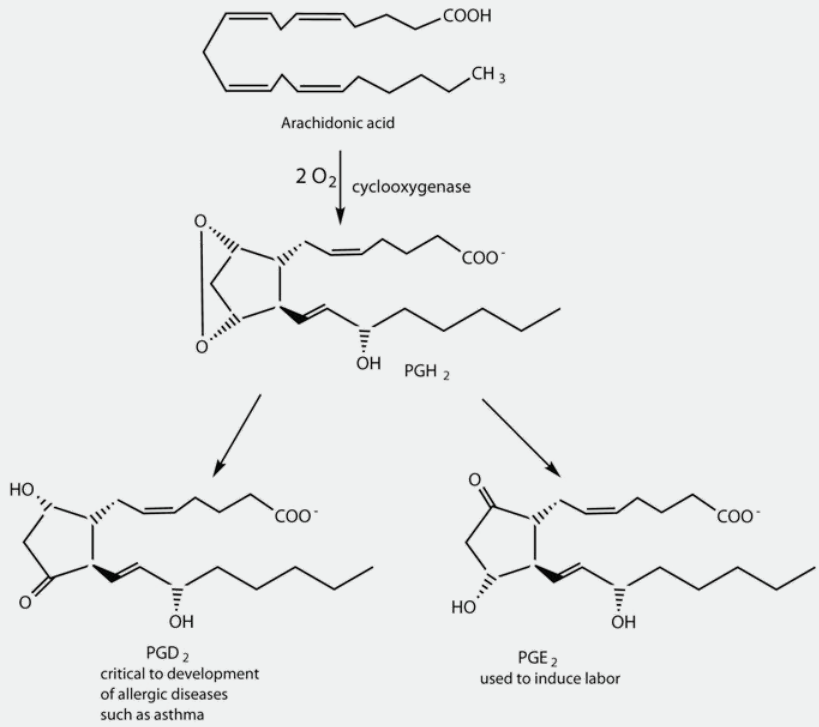
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
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 **14.2.2*a***). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure **14.2.2*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.

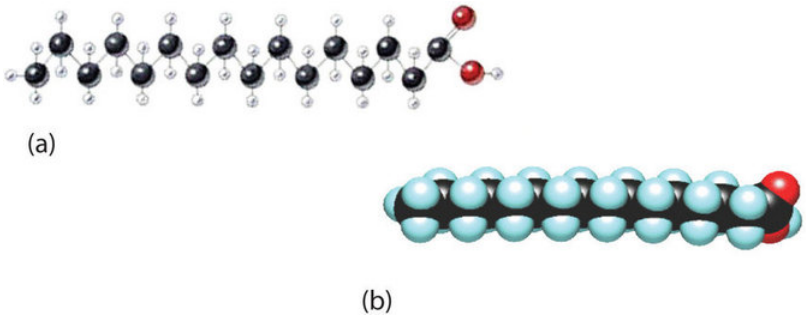
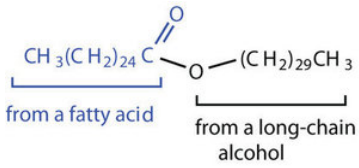


Figure **14.2.2**: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Myricyl cerotate
(found in carnauba wax)

Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

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14.3: Fats and Oils

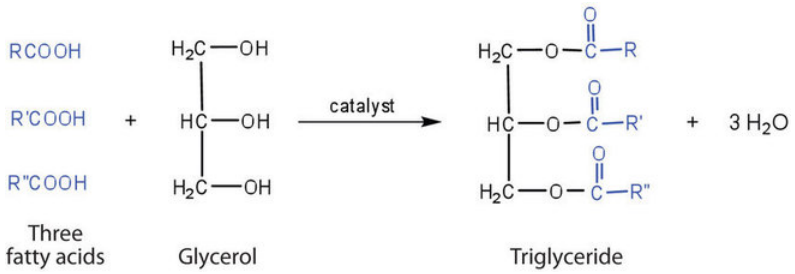
Learning Objectives

- Explain why fats and oils are referred to as triglycerides.
- Explain how the fatty acid composition of the triglycerides determines whether a substance is a fat or oil.
- Describe the importance of key reactions of triglycerides, such as hydrolysis, hydrogenation, and oxidation.

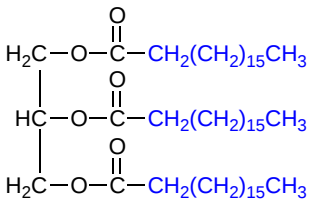
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

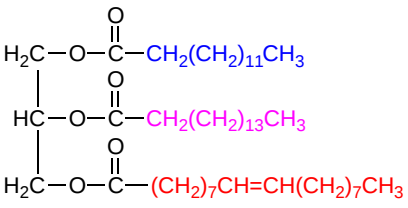
Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



Tristearin
a simple triglyceride



a mixed triglyceride

A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table **14.3.1** shows the fatty acid compositions of some common

fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

Table **14.3.1**: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil†	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

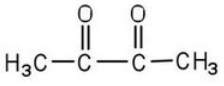
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

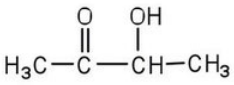
Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Physical Properties of Fats and Oils

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



Diacetyl

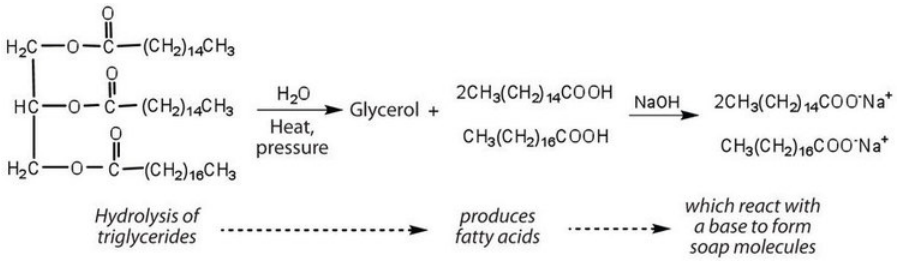


3-hydroxy-2-butanone

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

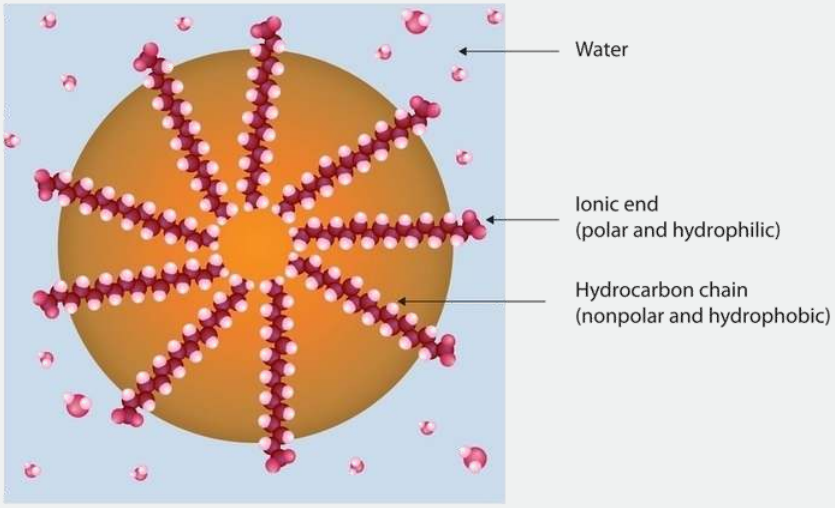
Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):



Looking Closer: Soaps

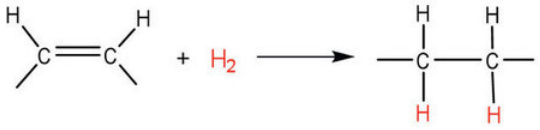
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.



Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer “gluing” the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

The double bonds in fats and oils can undergo hydrogenation and also oxidation. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry. Chemically, it is essentially identical to the catalytic hydrogenation reaction described for alkenes.



In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out. Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

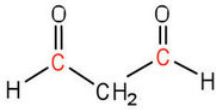
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the opening essay. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the ester bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit



in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.



Malonaldehyde

Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

Summary

Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

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14.4: Membranes and Membrane Lipids

Learning Objectives

- Identify the distinguishing characteristics of membrane lipids.
- Describe membrane components and how they are arranged.

All living cells are surrounded by a cell membrane. Plant cells (Figure **14.4.1*A***) and animal cells (Figure **14.4.1*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.

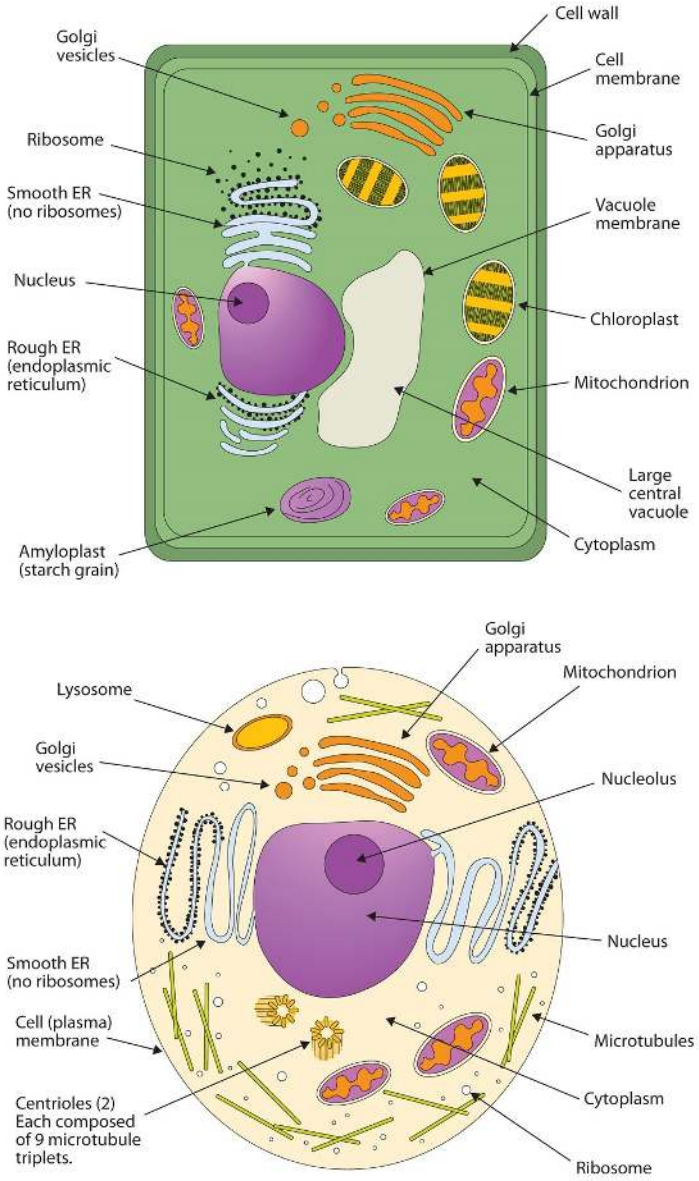


Figure **14.4.1**: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

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 **14.4.2**).

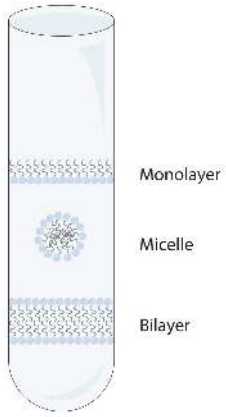


Figure **14.4.2**: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

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 **14.4.3**).

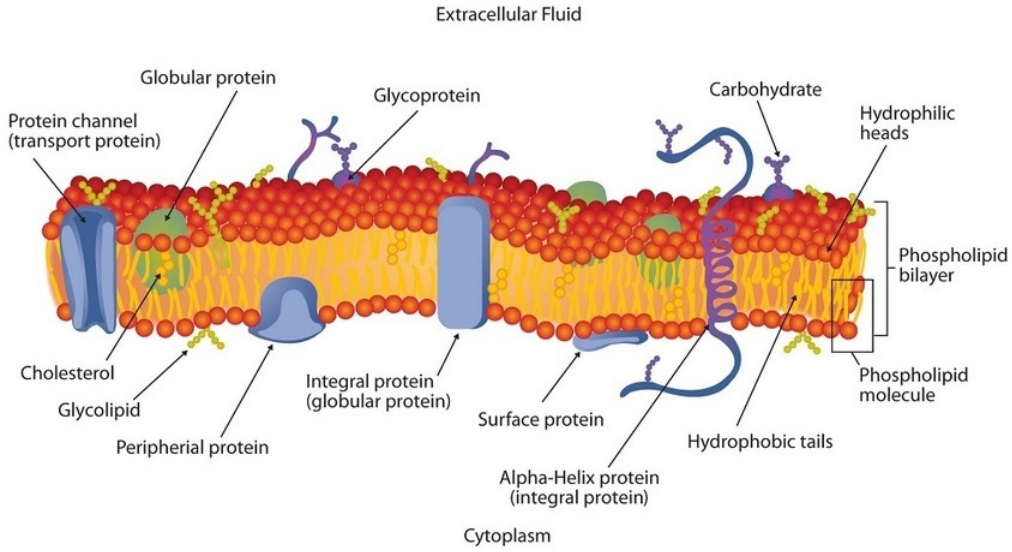


Figure **14.4.3**: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

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 **14.4.4**.

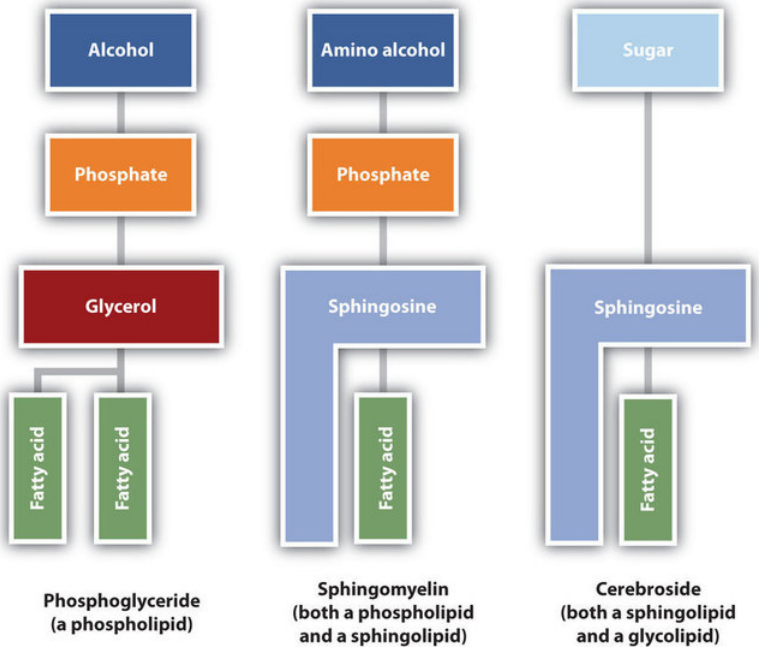


Figure **14.4.4**: Component Structures of Some Important Membrane Lipids

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 **14.4.5**) is attached to the third carbon atom of glycerol (part (b) of Figure **14.4.5**). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure **14.4.5**).

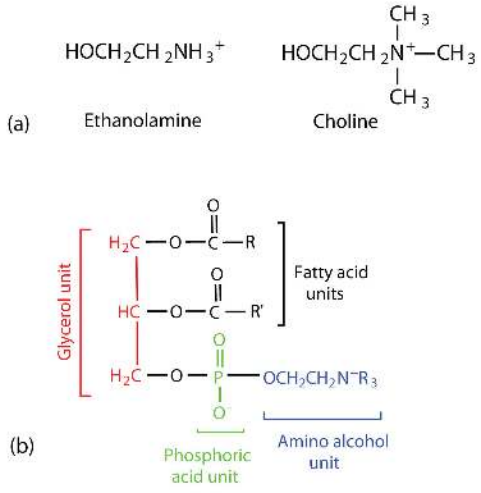
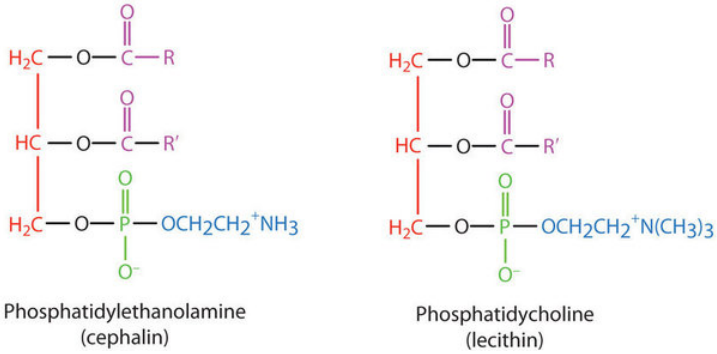


Figure **14.4.5**: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

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 **14.4.6**). 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.

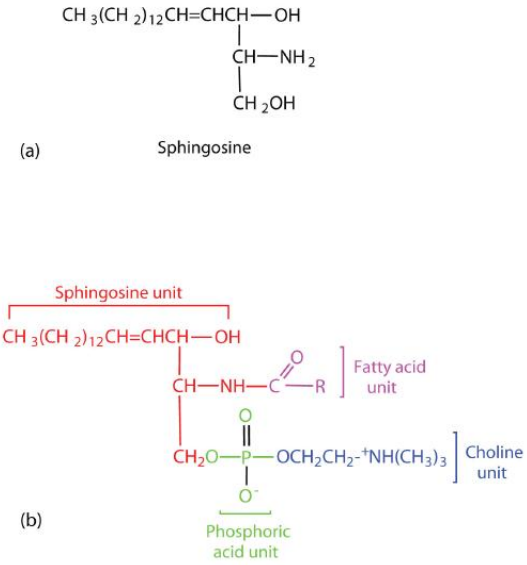


Figure **14.4.6**: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

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 **14.4.7**). 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.

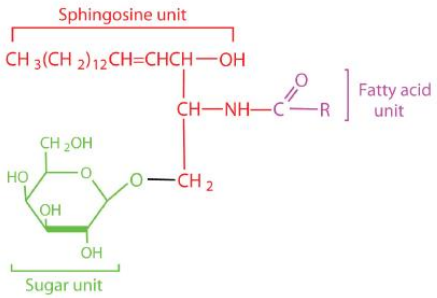


Figure 14.4.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

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 14.4.3). 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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14.5: Steroids

Learning Objectives

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).

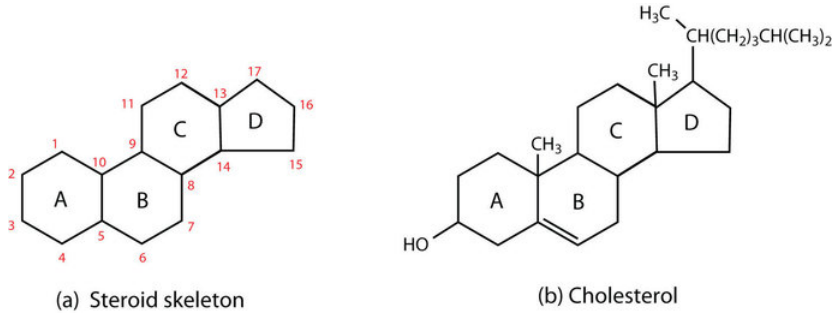


Figure 14.5.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure 14.5.1*a*. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 14.5.1*b*) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure 14.5.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



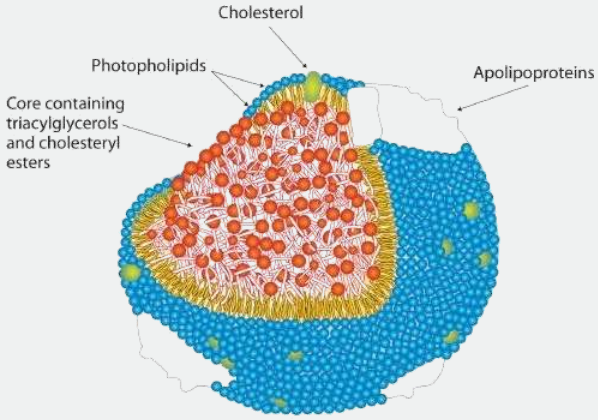
Figure 14.5.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.



Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

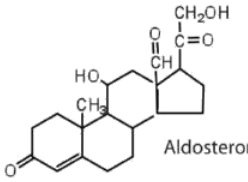
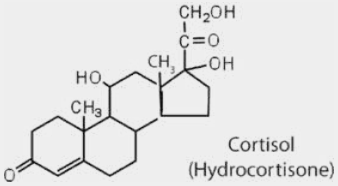
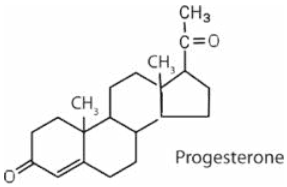
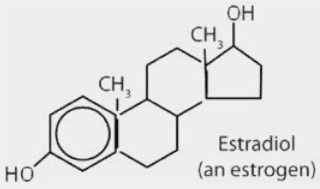
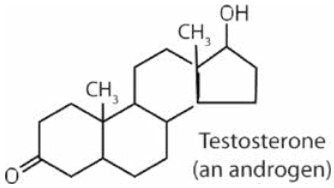
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

Steroid Hormones

Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

The adrenocortical hormones, such as aldosterone and cortisol (Table **14.5.1**), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table **14.5.1**: Representative Steroid Hormones and Their Physiological Effects

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle
 Testosterone (an androgen)	stimulates and maintains male sex characteristics

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex

hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure **14.5.3**) and an amine such as the amino acid glycine (part (b) of Figure **14.5.3**). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

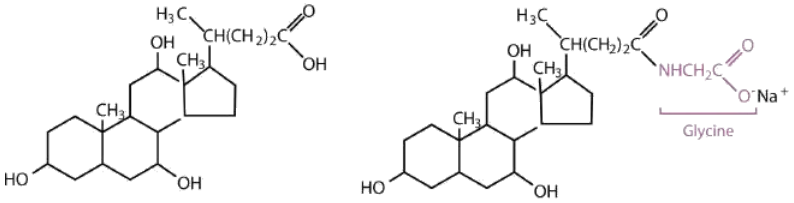


Figure **14.5.3** Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

Because they contain both hydrophobic and hydrophilic groups, bile salts are highly effective detergents and emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

> Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver's bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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14.S: Lipids (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Lipids, found in the body tissues of all organisms, are compounds that are more soluble in organic solvents than in water. Many of them contain **fatty acids**, which are carboxylic acids that generally contain an even number of 4–20 carbon atoms in an unbranched chain. **Saturated fatty acids** have no carbon-to-carbon double bonds. **Monounsaturated fatty acids** have a single carbon-to-carbon double bond, while **polyunsaturated fatty acids** have more than one carbon-to-carbon double bond. Linoleic and linolenic acid are known as **essential fatty acids** because the human body cannot synthesize these polyunsaturated fatty acids. The lipids known as **fats** and **oils** are triacylglycerols, more commonly called **triglycerides**—esters composed of three fatty acids joined to the trihydroxy alcohol glycerol. Fats are triglycerides that are solid at room temperature, and oils are triglycerides that are liquid at room temperature. Fats are found mainly in animals, and oils found mainly in plants. *Saturated triglycerides* are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglycerides* contain a higher proportion of unsaturated fatty acid chains.

Saponification is the hydrolysis of a triglyceride in a basic solution to form glycerol and three carboxylate anions or soap molecules. Other important reactions are the hydrogenation and oxidation of double bonds in unsaturated fats and oils.

Phospholipids are lipids containing phosphorus. In **phosphoglycerides**, the phosphorus is joined to an amino alcohol unit. Some phosphoglycerides, like lecithins, are used to stabilize an **emulsion**—a dispersion of two liquids that do not normally mix, such as oil and water. **Sphingolipids** are lipids for which the precursor is the amino alcohol sphingosine, rather than glycerol. A **glycolipid** has a sugar substituted at one of the OH groups of either glycerol or sphingosine. All are highly polar lipids found in cell membranes.

Polar lipids have dual characteristics: one part of the molecule is ionic and dissolves in water; the rest has a hydrocarbon structure and dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic** (literally, “water loving”) and the nonpolar part as **hydrophobic** (“water fearing”). When placed in water, polar lipids disperse into any one of three arrangements: *micelles*, *monolayers*, and *bilayers*. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

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CHAPTER OVERVIEW

15: Amino Acids, Proteins, and Enzymes

15.1: Prelude to Amino Acids, Proteins, and Enzymes

15.2: Properties of Amino Acids

15.3: Reactions of Amino Acids

15.4: Peptides

15.5: Proteins

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15.1: Prelude to Amino Acids, Proteins, and Enzymes

The 1923 Nobel Prize in Medicine or Physiology was awarded to Frederick Grant Banting and John James Richard Macleod for their discovery of the protein *insulin*. In 1958, the Nobel Prize in Chemistry was awarded to Frederick Sanger for his discoveries concerning the structure of proteins and, in particular, the structure of insulin. What is so important about insulin that two Nobel Prizes have been awarded for work on this protein?

Insulin is a hormone that is synthesized in the pancreas. Insulin stimulates the transport of glucose into cells throughout the body and the storage of glucose as glycogen. People with diabetes do not produce insulin or use it properly. The isolation of insulin in 1921 led to the first effective treatment for these individuals.



Figure **15.1.1**: Insulin pump, showing an infusion set loaded into spring-loaded insertion device. A reservoir is attached to the infusion set (shown here removed from the pump). (Public Domain; User:David-i98).

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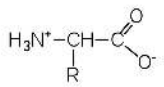
15.2: Properties of Amino Acids

Learning Objectives

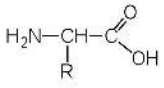
- To recognize amino acids and classify them based on the characteristics of their side chains.

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

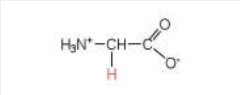
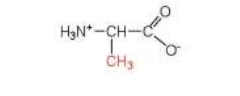
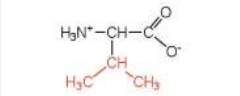
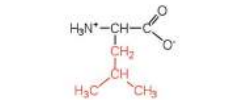
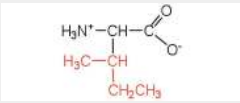
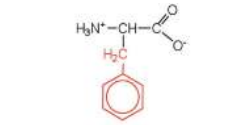
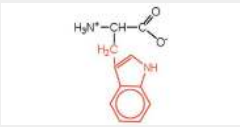
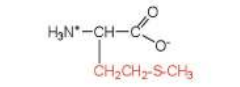
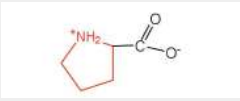
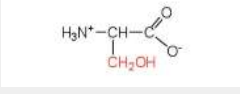
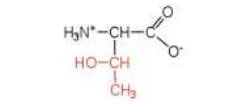
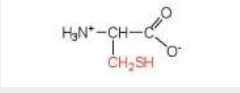


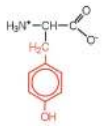
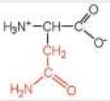
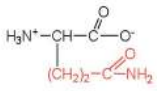
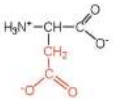
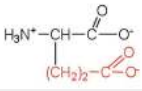
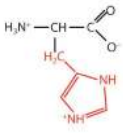
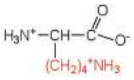
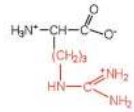
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

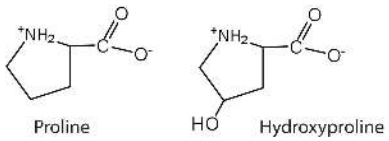
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound 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 **15.2.1**.

Table **15.2.1**: 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
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

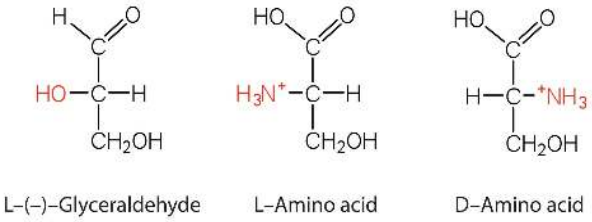
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Configuration

Notice in Table **15.2.1** 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.

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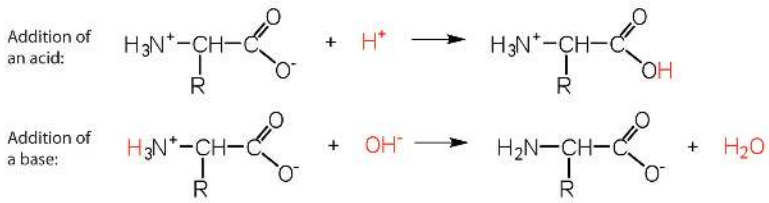
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15.3: Reactions of Amino Acids

Learning Objectives

- To explain how an amino acid can act as both an acid and a base.

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.

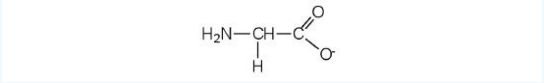


Example 15.3.1

a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

Solution

a. The base removes H^+ from the protonated amine group.



- The acid adds H^+ to the carboxylate group.



Exercise 15.3.1

a. Draw the structure for the cation formed when valine (at neutral pH) reacts with an acid.
b. Draw the structure for the anion formed when valine (at neutral pH) reacts with a base.

The particular pH at which a given amino acid exists in solution as a zwitterion is called the isoelectric point (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have isoelectric points ranging from 5.0 to 6.5. The basic amino acids (which have positively charged side chains at neutral pH) have relatively high examples. Acidic amino acids (which have negatively charged side chains at neutral pH) have quite low examples (Table 15.3.1).

Table 15.3.1: ExampIes of Some Representative Amino Acids

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7
threonine	polar, uncharged	6.5
arginine	positively charged (basic)	10.8
histidine	positively charged (basic)	7.6
lysine	positively charged (basic)	9.8
aspartic acid	negatively charged (acidic)	3.0
glutamic acid	negatively charged (acidic)	3.2

Amino acids undergo reactions characteristic of carboxylic acids and amines. The reactivity of these functional groups is particularly important in linking amino acids together to form peptides and proteins, as you will see later in this chapter. Simple chemical tests that are used to detect amino acids take advantage of the reactivity of these functional groups. An example is the ninhydrin test in which the amine functional group of α-amino acids reacts with ninhydrin to form purple-colored compounds. Ninhydrin is used to detect fingerprints because it reacts with amino acids from the proteins in skin cells transferred to the surface by the individual leaving the fingerprint.



Ninhydrin



Summary

Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

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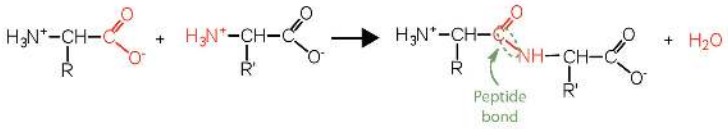
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15.4: Peptides

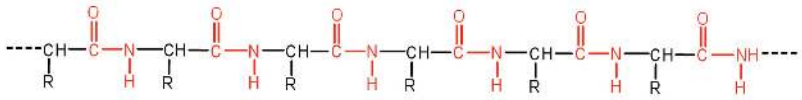
Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

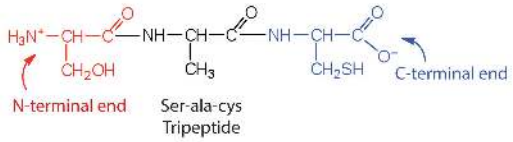
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:



An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.



A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.



The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

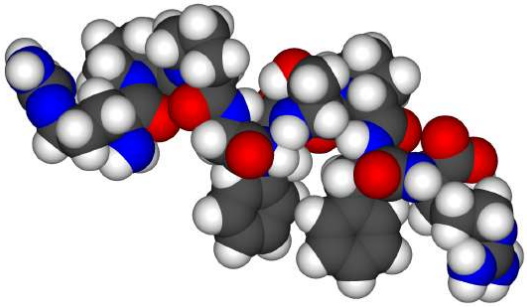


Figure **15.4.1**: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure **15.4.1**) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of “incorrect” amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That “minor” error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

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15.5: Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain 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 15.5.1.

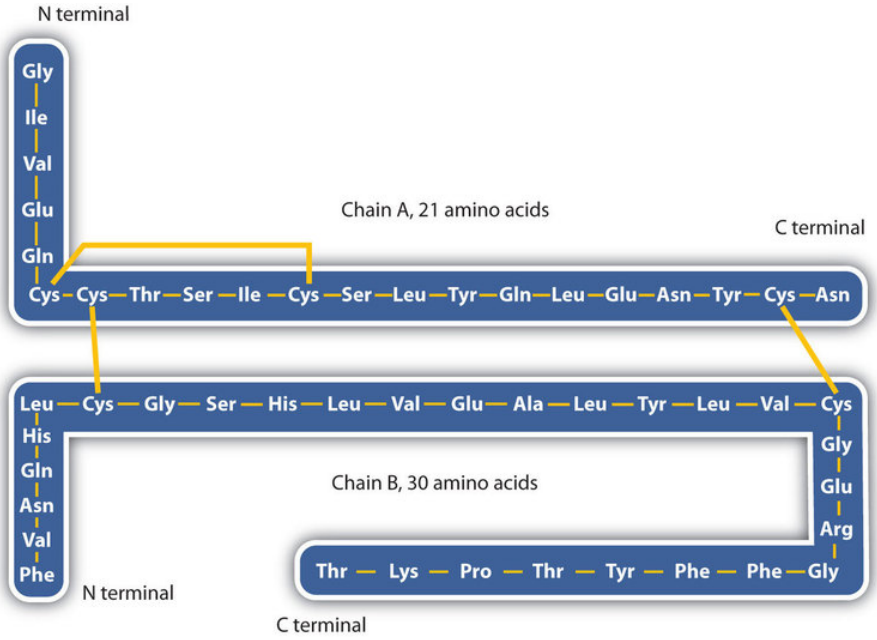


Figure 15.5.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 15.5.2). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

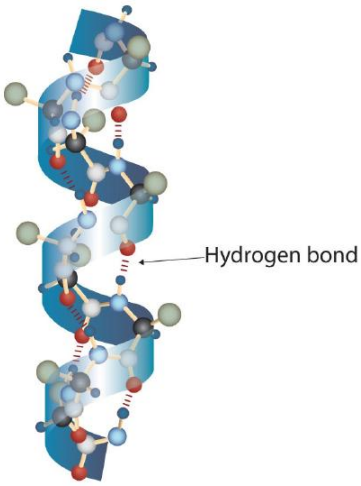


Figure 15.5.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—

and are connected by *interchain* hydrogen bonding (Figure **15.5.3**). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

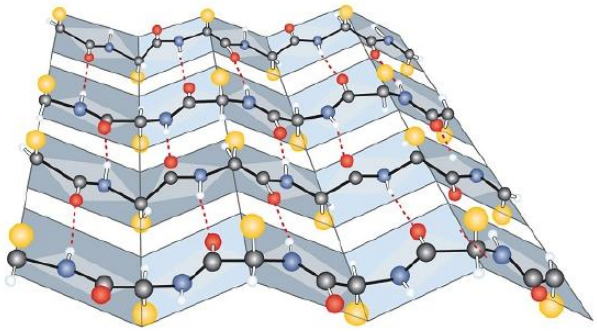


Figure **15.5.3**: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure **15.5.4** shows a depiction of the three-dimensional structure of insulin.

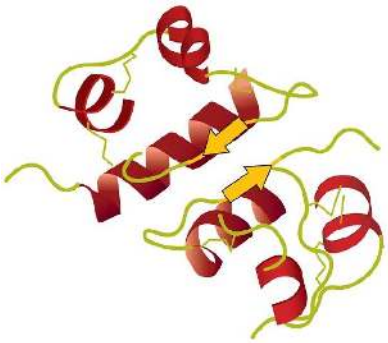
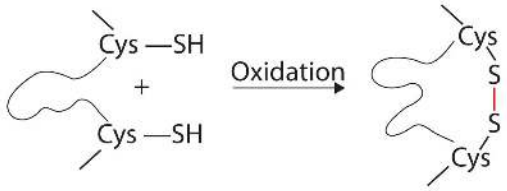


Figure **15.5.4**: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure **15.5.5**).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure **15.5.5**).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure **15.5.5**). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure **15.5.1**) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure **15.5.5**). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

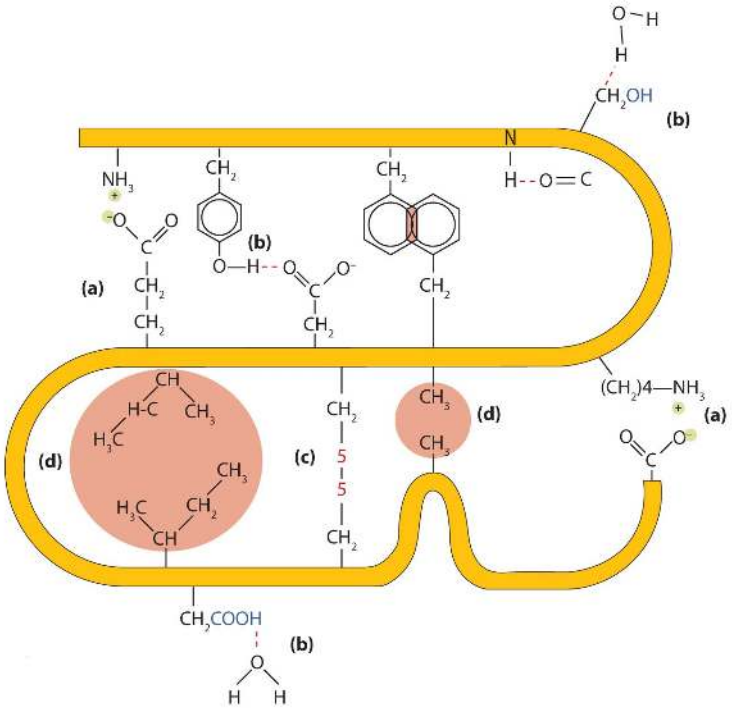


Figure **15.5.5**: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure **15.5.6**). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure **15.5.7**.

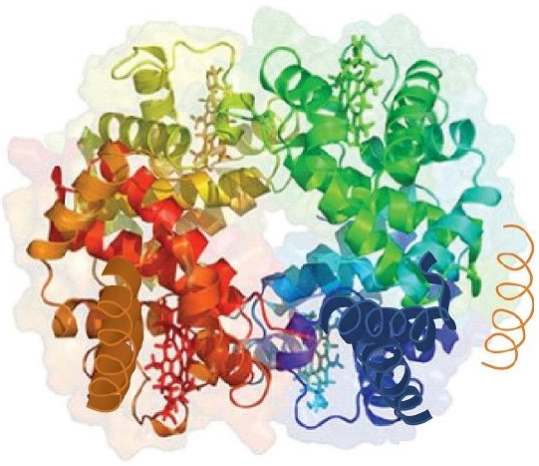


Figure **15.5.6** The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(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).

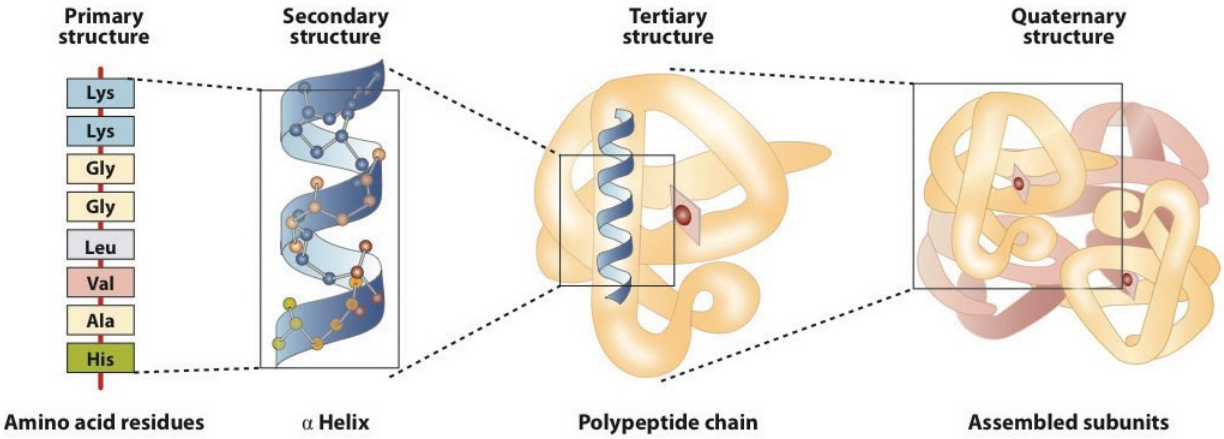


Figure **15.5.7**: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

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 **15.5.1**).

Figure **15.5.1**: 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 15.5.8). 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.

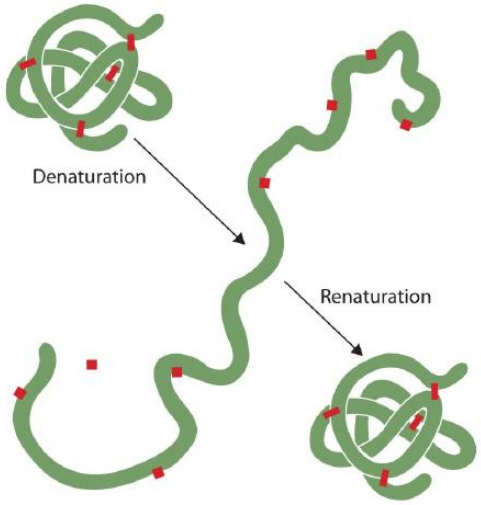


Figure 15.5.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

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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