CHEM100

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This text was compiled on 03/12/2025

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Detailed Licensing

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing***.

CHAPTER OVERVIEW

1: Introductory Information

1.1: Scope of Chemistry

Figure 1.1.1 (Credit: User:Phanton/Wikipedia; Source: https://commons.wikimedia.org/wiki/File:Decorative_Soaps.jpg; License: Public Domain)

How does soap relate to chemistry?

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

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

What is Chemistry?

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

Figure 1.1.2: Chemical reactions in the leaves of deciduous trees cause them to change color from green to red, orange, or yellow before dropping to the ground. (Credit: User:Jongleur100/Wikimedia Commons; Source: https://commons.wikimedia.org/wiki/File:Country_lane.jpg; License: Public Domain)

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

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

Figure 1.1.3: *Rusting artillery shells.* (Courtesy of the US Marine Corps, Source: http://commons.wikimedia.org/wiki/File:USMC-060507-M-7799R-003.jpg; License: Public Domain)

Summary

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

Review

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

Explore More

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

- **1.1: Scope of Chemistry** by CK-12 Foundation is licensed CK-12. Original source: https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/.

1.2: Areas of Chemistry

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

- Physical chemistry
- Organic chemistry
- Inorganic chemistry
- Analytical chemistry
- Biochemistry

Physical Chemistry

Physical chemistry is the study of macroscopic properties, atomic properties, and phenomena in chemical systems. As examples, a physical chemist may study the rates of chemical reactions, the energy transfers that occur in reactions, or the physical structure of materials at the molecular level.

Organic Chemistry

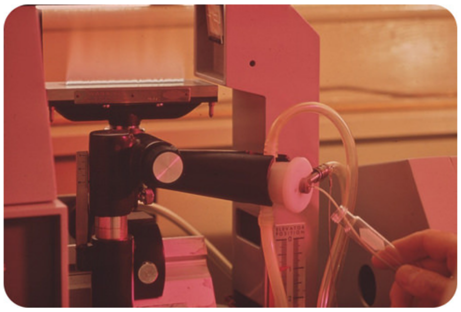
Organic chemistry is the study of chemicals containing carbon. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far). Most chemicals found in every living organism are based on carbon.

Inorganic Chemistry

Inorganic chemistry is the study of chemicals that do not, in general, contain carbon. Inorganic chemicals are commonly found in rocks and minerals. One current important area of inorganic chemistry deals with the design and properties of materials involved in energy and information technology.

Analytical Chemistry

Analytical chemistry is the study of the composition of matter. It focuses on separating, identifying, and quantifying chemicals in samples of matter. An analytical chemist may use complex instruments to analyze an unknown material, in order to determine its various components.



: Measurement of trace metals using atomic spectroscopy. (Courtesy of Bill Shrout, Environmental Protection Agen
ikimedia.org/wiki/File:EPA_GULF_BREEZE_LABORATORY,_THE_MICROBIOLOGY_LAB._AN_ATOMIC_ABSORPTION_SYSTEM,_WHICH_MEASURES_MINUTE_QUA
9.tif(opens in new window); License: Public Domain)

Biochemistry

Biochemistry is the study of chemical processes that occur in living things. Research may cover basic cellular processes up to understanding disease states, so that better treatments can be developed.

Figure 1.2.2: Measuring hormone concentrations. (Courtesy of Fred W. Baker III, U.S. Department of Defense; Source: http://commons.wikimedia.org/wiki/File:Defense.gov_photo_essay_090506-D-1852B-019.jpg(opens in new window); License: Public Domain)

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

Summary

- Five areas of chemistry are described:
  - Physical chemistry
  - Organic chemistry
  - Inorganic chemistry
  - Analytical chemistry
  - Biochemistry

Review

Match the project with the proper chemistry discipline.

Match the project with the proper chemistry discipline.

a. measuring mercury in seawater	1. biochemistry
b. studying enzymes in cells	2. organic chemistry
c. measuring the electrical properties of solutions	3. inorganic chemistry
d. synthesizing new carbon compounds	4. physical chemistry
e. making new compounds for energy processes	5. analytical chemistry

Explore More

1. Do an internet search using one of the five chemistry areas as a search term. List two significant contributions made to chemistry by that area.

1.3: 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 1.3.2: *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 1.3.3: *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 1.3.4: *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?

1.4: Matter, Mass, and Volume

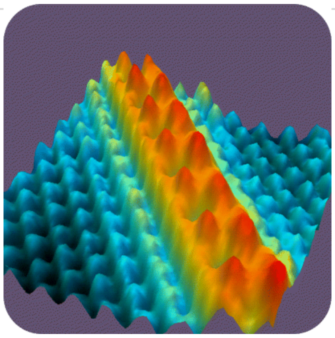


Figure 1.4.1 (Credit: Courtesy of L.J. Whitman, J.A. Stroscio, R.A. Dragoset, R.J. Celotta, and the National Institute of Standards and Technology; Source: NIST, Physical Measurement Laboratory, Scanning Tunneling Microscope(opens in new window) [www.nist.gov]; License: Public Domain)

Can you guess what this colorful image shows?

Believe it or not, it actually depicts individual atoms of cesium (reddish-orange) on a surface of gallium arsenide molecules (blue). The image was created with an extremely powerful microscope, called a scanning tunneling microscope. This is one of a few types of microscope that can make images of atoms, the basic building blocks of matter.

What’s the Matter?

Matter is all the “stuff” that exists in the universe. Everything you can see and touch is made of matter, including you! The only things that aren’t matter are forms of energy, such as light and sound. In science, **matter** is defined as anything that has mass and volume. Mass and volume measure different aspects of matter.

Mass

Mass is a measure of the amount of matter in a substance or an object. The basic SI unit for mass is the kilogram (kg), but smaller masses may be measured in grams (g). To measure mass, you would use a balance. In the lab, mass may be measured with a triple beam balance or an electronic balance, but the old-fashioned balance pictured below may give you a better idea of what mass is. If both sides of this balance were at the same level, it would mean that the fruit in the left pan has the same mass as the iron object in the right pan. In that case, the fruit would have a mass of 1 kg, the same as the iron. As you can see, however, the fruit is at a higher level than the iron. This means that the fruit has less mass than the iron, that is, the fruit's mass is less than 1 kg.

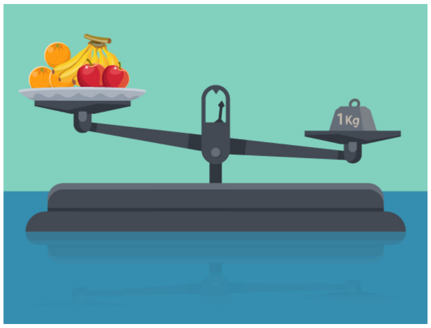


Figure 1.4.2 (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials License(opens in new window))

Q: Refer to the picture above. If the fruit were at a lower level than the iron object, what would be the mass of the fruit?

A: The mass of the fruit would be greater than 1 kg.

Mass vs. Weight

Mass is commonly confused with weight. The two are closely related, but they measure different things. Whereas mass measures the amount of matter in an object, weight measures the force of gravity acting on an object. The force of gravity on an object depends on its mass but also on the strength of gravity. If the strength of gravity is held constant (as it is all over Earth), then an object mass is directly proportional to the objects weight, so a greater mass also has a greater weight.

Q: With Earth’s gravity, an object with a mass of 1 kg has a weight of 2.2 lb. How much does a 10 kg object weigh on Earth?

A: A 10 kg object weighs ten times as much as a 1 kg object: 10 × 2.2 lb = **22 lb**

Volume

Volume is a measure of the amount of space that a substance or an object takes up. The basic SI unit for volume is the cubic meter (m^3), but smaller volumes may be measured in cm^3, and liquids may be measured in liters (L) or milliliters (mL). How the volume of matter is measured depends on its state.

- The volume of a liquid is measured with a measuring container, such as a measuring cup or graduated cylinder.
- The volume of a gas depends on the volume of its container: gases expand to fill whatever space is available to them.
- The volume of a regularly shaped solid can be calculated from its dimensions. For example, the volume of a rectangular solid is the product of its length, width, and height.
- The volume of an irregularly shaped solid can be measured by the displacement method. You can read below how this method works.

Calculating Volume from Dimensions

Q: How could you find the volume of air in an otherwise empty room?

A: If the room has a regular shape, you could calculate its volume from its dimensions. For example, the volume of a rectangular room can be calculated with the formula:

Volume = length × width × height

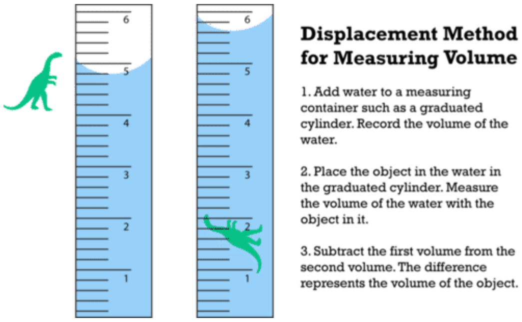
If the length of the room is 5.0 meters, the width is 3.0 meters, and the height is 2.5 meters, then the volume of the room is:

Volume = 5.0 m × 3.0 m × 2.5 m = 37.5 m3

Measuring Volume Using the Displacement Method

The following video shows how the volume of an irregular shaped object, like your science teacher can be measured by the displacement method.

Q: What is the volume of the dinosaur in the diagram below?



Displacement Method for Measuring Volume

1. Add water to a measuring container such as a graduated cylinder. Record the volume of the water.
2. Place the object in the water in the graduated cylinder. Measure the volume of the water with the object in it.
3. Subtract the first volume from the second volume. The difference represents the volume of the object.

Figure 1.4.3 (Credit: Christopher AuYeung; Source: CK-12 Foundation; License: CK-12 Curriculum Materials License(opens in new window))

A: The volume of the water alone is 4.8 mL. The volume of the water and dinosaur together is 5.6 mL. Therefore, the volume of the dinosaur alone is 5.6 mL – 4.8 mL = 0.8 mL.

Summary

- Matter is all the “stuff” that exists in the universe. It has both mass and volume.
- Mass measures the amount of matter in a substance or an object. The basic SI unit for mass is the kilogram (kg).
- Volume measures the amount of space that a substance or an object takes up. The basic SI unit for volume is the cubic meter (m^3).

Review

1. How do scientists define matter?
2. What is mass? What is the basic SI unit of mass?
3. What does volume measure? Name two different units that might be used to measure volume.
4. Explain how to use the displacement method to find the volume of an irregularly shaped object.

1.5: States of Matter

Figure 1.5.1 (Credit: Iceberg: Courtesy of Rear Admiral Harley D. Nygren, NOAA; Beach: User:Wicki/Wikimedia Commons; Volcano: Courtesy of E. Klett, US Fish and Wildlife Service; Source: Iceberg: http://commons.wikimedia.org/wiki/File:Ice_berg.jpg(opens in new window); Beach: http://commons.wikimedia.org/wiki/File:Ocean_Spokojny.JPG(opens in new window); Volcano: http://commons.wikimedia.org/wiki/File:Dds40-097_large.jpeg(opens in new window); License: Public Domain)

Why is the state of water different in each picture?

Water can take many forms. At low temperatures (below 0^oC), water is a solid. When at "normal" temperatures (between 0^oC and 100^oC), it is a liquid. At temperatures above 100^oC, water is a gas (steam).

The state of water depends on the temperature. Each state (solid, liquid, and gas) has its own unique set of physical properties.

Matter and its States

Matter typically exists in one of three states: **solid**, **liquid**, or **gas**. There is a fourth state of matter called **plasma**, which rarely exists on earth, but we will omit this from our current discussion. The state 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.

Liquid

Liquids have the following characteristics:

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

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), which is a property that all liquids exhibit. Mercury has a relatively high surface tension, and this makes it very unique. Here you can see mercury in its common liquid form.

Figure 1.5.2: *Mercury.* (Courtesy of the EPA; Source: http://commons.wikimedia.org/wiki/File:Mercury-element.jpg(opens in new window); License: Public Domain)

If we heat liquid mercury to its boiling point of 357^oC, and contain it under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.

Gas

Gases have the following characteristics:

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

Solid

Solids are defined by the following characteristics:

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

If we were to cool a sample of liquid mercury to its freezing point of -39^{o}C, and had it contained under the right pressure conditions, we would notice all of the liquid particles would go into the solid state.

As you can see in the video, 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.

Plasma

Plasma is a state of matter that resembles a gas but has certain properties that gases do not have. Like a gas, plasma consists of particles of matter that can pull apart and spread out, so it lacks a fixed volume and a fixed shape. Unlike a gas, plasma can conduct electricity and respond to a magnetic field. That’s because plasma consists of electrically charged particles called ions, instead of uncharged particles such as atoms or molecules.

Plasma are defined by the following characteristics:

- particles are charged ions and free electrons
- no definite shape
- no definite volume
- conducts electricity
- responds to magnetic field

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 their container.
- Gases have no definite shape or volume.

Review

1. How many states of matter are there?
2. What is a solid?
3. What is a liquid?
4. What is a gas?

CHAPTER OVERVIEW

2: Atoms and Elements

2.1: Cutting gold until you get atoms

Take a block of solid gold. Cut it in half. Now there are two smaller pieces of gold. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of gold. It should be obvious that the pieces are still gold; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the gold into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of gold? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC by Democritus and other ancient Greek philosophers (Figure $2.1.1$).

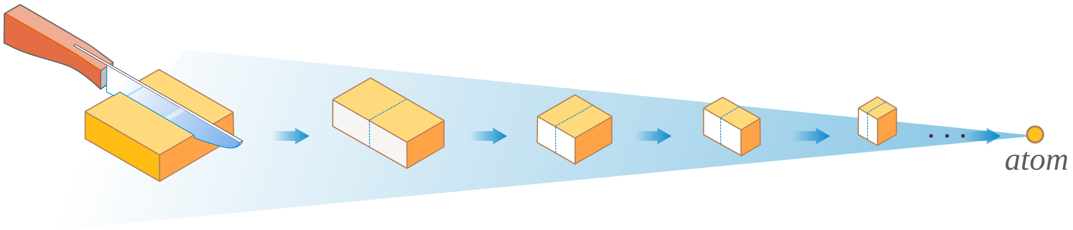


Figure $2.1.1$: Democritus argued that matter, like an gold block, cannot be repeatedly cut in half perpetually. At some point, a limit is reached before the substance can no longer be called "gold"; this is the atomic limit. (CC BY-NC; Ümit Kaya via LibreTexts)

2.2: The Atom

Learning Objectives

- State the **modern atomic theory**.
- Define and differentiate the terms **atom** and **element**.
- Identify the location and charge of protons, neutrons, and electrons.
- Remember and use the different symbols that represent protons, neutrons, and electrons.

Pure gold is an example of an element. An **element** is a pure substance that cannot be broken down (by a chemical process) into simpler substances. In the previous section you saw an illustration of a large piece of the element gold broken down into smaller and smaller pieces until the smallest possible piece. The smallest piece of an element that maintains the identity of that element is called an **atom**. In the case of the sample of gold, the large pieces can be called the element gold. The smallest piece of the element gold is an atom of gold. So what we mean when we say the element can't be broken down into simpler substances is that all of the pieces of the element share the same name and properties. All the pieces of the element gold are still gold. Some substances, like water for example, are made of more than one type of element. They can be broken down into smaller pieces that do not share the same element name. Those substances will be covered in a later chapter.

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

Because everything is made of atoms, their study is useful to understanding how the world works. The concept that atoms play a fundamental role in chemistry is formalized by the **modern atomic theory**. It consists of three parts:

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

These concepts form the basis of chemistry. Atoms themselves are composed of smaller parts called *subatomic particles*. The first part of an atom to be discovered was the electron, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The proton is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The neutron is a subatomic particle with about the same mass as a proton, but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table $2.2.1$ summarizes the properties of these three subatomic particles.

Table $2.2.1$: Properties of the Three Subatomic Particles

Name	Symbol	Charge
Proton	p^+	1+
Neutron	n, n^0	none
Electron	e^-	1−

How are these particles arranged in atoms? They are not arranged at random. The protons and neutrons are collected in the center of an atom, in a region called the nucleus of the atom (plural *nuclei*). The electrons spend their time in constant motion outside the nucleus. (Figure $2.2.1$).

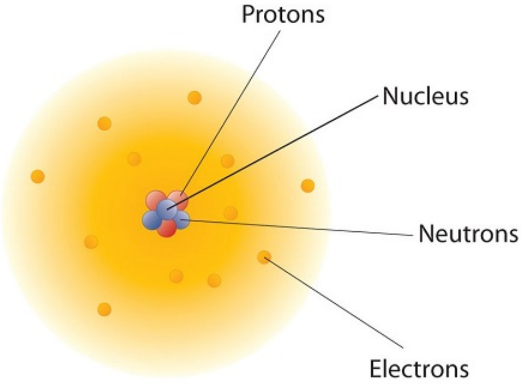


Figure 2.2.1: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

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

Atoms of the same element can have different numbers of neutrons, however. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called **isotopes**. Most naturally occurring elements exist as isotopes. The next section will cover isotopes in more depth.

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

✓ Example 2.2.1

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

Solution

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

? Exercise 2.2.1

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer

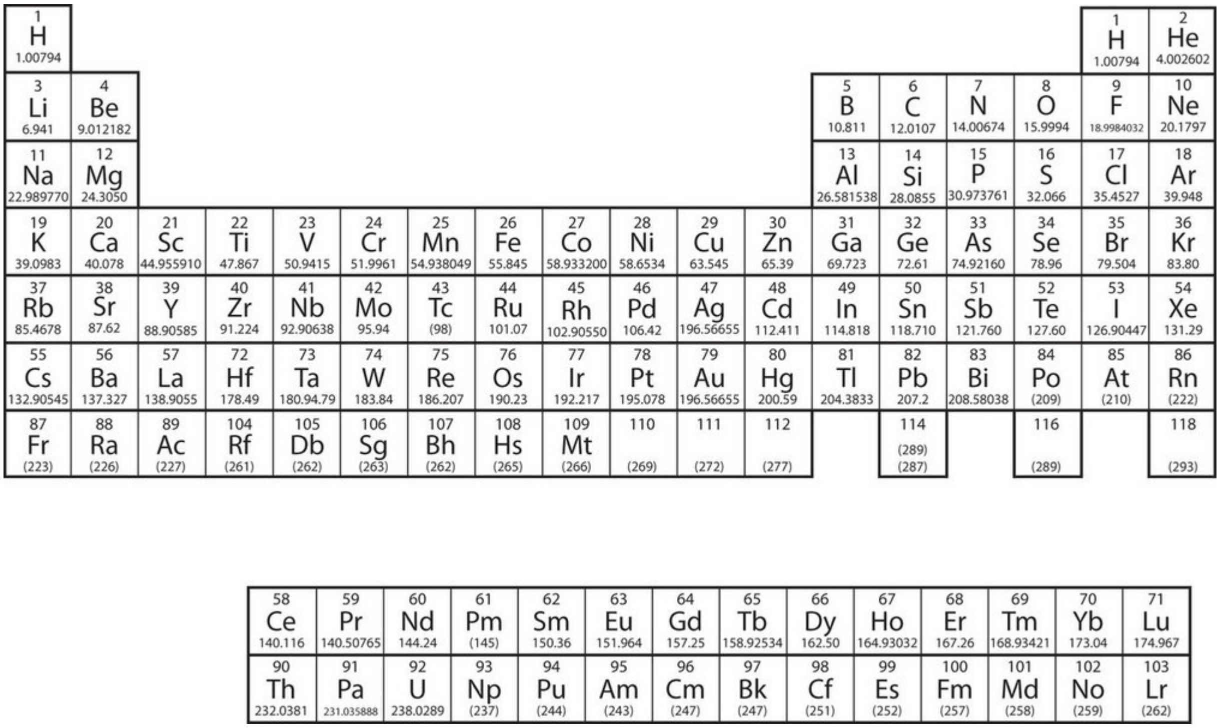
Atomic number = 50, mass number = 118

When referring to an atom, we simply use the element's name: the term *sodium* refers to the element as well as an atom of sodium. But it can be unwieldy to use the name of elements all the time. Instead, chemistry defines a symbol for each element. The atomic symbol is a one- or two-letter representation of the name of an element. By convention, the first letter of an element's symbol is always capitalized, while the second letter (if present) is lowercase. Thus, the symbol for hydrogen is H, the symbol for sodium is Na, and the symbol for nickel is Ni. Most symbols come from the English name of the element, although some symbols come from an element's Latin name. (The symbol for sodium, Na, comes from its Latin name, *natrium*.) Table 2.2.2 lists some common elements and their symbols. You should memorize the symbols in Table 2.2.2, as this is how we will be representing elements throughout chemistry.

Table 2.2.2: Names and Symbols of Common Elements

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

The elements are grouped together in a special chart called the periodic table of all the elements. A simple periodic table is shown in Figure 2.2.2. The elements on the periodic table are listed in order of ascending atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (Chapter 8). One immediate use of the periodic table helps us identify metals and nonmetals. Nonmetals are in the upper right-hand corner of the periodic table, on one side of the heavy line splitting the right-side part of the chart. All other elements are metals.



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

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

Figure 2.2.1: A Simple Periodic Table

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Elements are represented by an atomic symbol.
- The periodic table is a chart that organizes all the elements.

2.3: The Atomic Number and Mass Number

Learning Objectives

- Define atomic number, mass number, and isotope.
- Use the atomic number and mass number to determine the number of protons, neutrons, and electrons in an atom.

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

Atoms are electrically *neutral*, meaning that the overall electric charge is zero. This is because the number of protons (positive charge) equals the number of electrons (negative charge). Therefore, the atomic number also provides the number of electrons. For example, helium has the atomic number 2, which tells us that there are 2 protons in the nucleus and 2 electrons outside of the nucleus. Sometimes atoms will gain or lose electrons resulting in a difference in the number of protons and electrons, which means the charge is no longer zero. Atoms that have a charge are called *ions* and will be discussed in more detail later.

As we learned previously, protons and neutrons, which are found in the nucleus of an atom, each have a mass of ~1 amu. Because an electron has negligible mass relative to that of a proton or a neutron, the majority of an atom's mass is in the nucleus. The **mass number** is defined as the total number of protons and neutrons in an atom:

$$\textbf{mass number} = \textbf{protons} + \textbf{neutrons}$$

Atoms of the same element always have the same number of protons, but often have different numbers of neutrons, therefore, different mass numbers. These atoms are called **isotopes** and will be discussed in more detail in the next chapter.

Example 2.3.1

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

Solution

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

Exercise 2.3.1

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer

Atomic number = 50, mass number = 118

Example 2.3.2:

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $^{56}_{26}\text{Fe}$

Solution

a. The symbol for this isotope is ${}^{235}_{92}\mathrm{U}$
b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

? Exercise 2.3.2

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

Answer

11 protons

Key Takeaways

- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- The mass number is the sum of the number of protons and neutrons.
- The number of neutrons in an atom can be determined by subtracting the atomic number from the mass number.

Contributors

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2.4: Isotopes and Nuclear Symbols

Learning Objectives

- Explain how isotopes differ from one another.
- Use nuclear symbols to identify numbers of protons and neutrons in an isotope.

Isotopes

As introduced previously, atoms of a specific element are distinguished from other elements by their atomic number, (the number of protons). Atoms of the same element always have the same number of protons, however, the number of neutrons can vary. **Isotopes** are atoms of the same element that contain *different* numbers of *neutrons*. This difference in neutron amount affects the mass number (A) but not the atomic number (Z). In a chemical laboratory, isotopes of an element appear and react the same. For this reason, it is difficult to distinguish between different isotopes. In contrast, nuclear scientists can identify and separate different types of atomic nuclei. The technology required for this process is more sophisticated that what could be found in a typical chemical laboratory.

Figure $2.4.1$ shows an easy way to represent isotopes with a **nuclear symbol**, which includes the atomic or element symbol (represented by X), the mass number, A, and the atomic number, Z. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

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

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

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 92 protons and 146 neutrons.

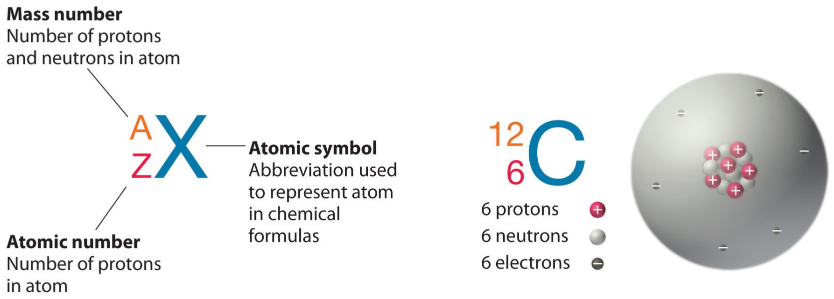


Figure 2.4.1: Nuclear Symbol. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons. (CC BY-NC-SA 4.0; anonymous by request)

Example 2.4.2

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $^{56}_{26}\text{Fe}$

Solution

a. The symbol for this isotope is $^{235}_{92}\text{U}$
b. This iron atom has 26 protons and $56 - 26 = 30$ neutrons.

? Exercise 2.4.2

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

Answer

11 protons

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

Most elements on the periodic table have at least two stable isotopes. For example, in addition to ^{12}C, a typical sample of carbon contains 1.11% $^{13}_{6}\text{C}$, with 7 neutrons and 6 protons, and a trace of $^{14}_{6}\text{C}$, with 8 neutrons and 6 protons. The nucleus of $^{14}_{6}\text{C}$ is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. There are about twenty elements that exist in only one isotopic form (sodium and fluorine are examples of these).

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 2.4.2 compares the three isotopes of hydrogen.

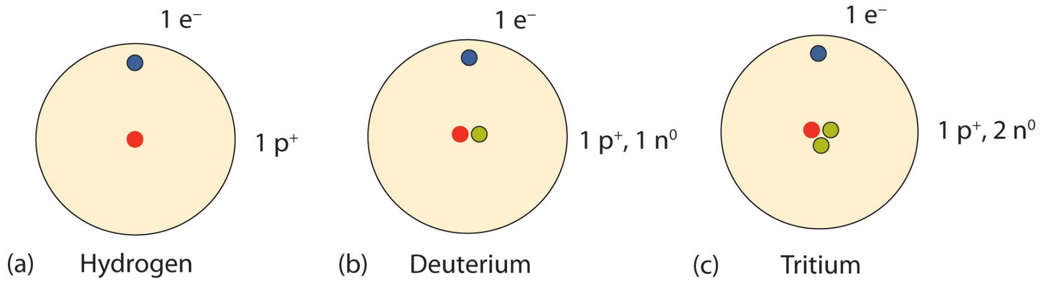


Figure 2.4.2: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

There are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. A/Z and symbol-mass formats can be used to display periodic table information. When viewing either of these two notations, isotopic differences can be obtained.

> *The discovery of isotopes required a minor change in Dalton's atomic theory. Dalton thought that all atoms of the same element were exactly the same.*

Look at the **A/Z formats** for the three isotopes of hydrogen in Table 2.4.1. Note how the atomic number (bottom value) remains the same while the atomic masses (top number) are varied. All isotopes of a particular element will vary in neutrons and mass. This variance in mass will be visible in the **symbol-mass format** of same isotopes as well.

Table 2.4.1

Common Name	A/Z formats	symbol-mass format	Expanded Name
Hydrogen	$^{1}_{1}\text{H}$	H-1	hydrogen-1
Deuterium	$^{2}_{1}\text{H}$	H-2	hydrogen-2
Tritium	$^{3}_{1}\text{H}$	H-3	hydrogen-3

Both A/Z or symbol-mass formats can be utilized to determine the amount of subatomic particles (protons, neutrons, and electrons) contained inside an isotope. When given either format, these mass values should be used to calculate the number of neutrons in the nucleus.

Concept Review Exercises

1. Why is the atomic number so important to the identity of an atom?
2. What is the relationship between the number of protons and the number of electrons in an atom?
3. How do isotopes of an element differ from each other?
4. What is the mass number of an element?
5. How can you determine the number of protons and neutrons from a nuclear symbol?

Answers

1. The atomic number defines the identity of an element. It describes the number of protons in the nucleus.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes of an element have the same number of protons but have different numbers of neutrons in their nuclei.
4. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.

Contributors and Attributions

-
- Elizabeth R. Gordon (Furman University)

CHAPTER OVERVIEW

3: Atomic Mass and Measurements

In 1983, an Air Canada airplane had to make an emergency landing because it unexpectedly ran out of fuel; ground personnel had filled the fuel tanks with a certain number of pounds of fuel, not kilograms of fuel. In 1999, the Mars Climate Orbiter spacecraft was lost whilst attempting to orbit Mars because the thrusters were programmed in terms of English units, even though the engineers built the spacecraft using metric units. In 1993, a nurse mistakenly administered 23 units of morphine to a patient rather than the "2–3" units prescribed (the patient ultimately survived). These incidents occurred because people were not paying attention to quantities.

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

3.1: Expressing Quantities

Learning Objective

- Express numbers in either standard notation or scientific notation.
- Write quantities with correct units.

Quantities have two parts: the number and the unit. The number tells "how many." It is important to be able to express numbers properly so that the quantities can be communicated properly.

Standard Notation

Standard notation is the straightforward expression of a number. Numbers such as 17, 101.5, and 0.00446 are expressed in standard notation. For relatively small numbers, standard notation is fine. However, for very large numbers, such as 306,000,000, or for very small numbers, such as 0.000000419, standard notation can be cumbersome because of the number of zeros needed to place nonzero numbers in the proper position.

Scientific Notation

Scientific notation is an expression of a number using powers of 10. Powers of 10 are used to express numbers that have many zeros:

Table 3.1.1 shows the powers of 10. Left side has 10 to a specific power and right side has the equation for the specified power.

10^0	= 1
10^1	= 10
10^2	= 100 = 10 × 10
10^3	= 1,000 = 10 × 10 × 10
10^4	= 10,000 = 10 × 10 × 10 × 10

and so forth.

The raised number to the right of the 10 indicates the number of factors of 10 in the original number. (Scientific notation is sometimes called *exponential notation*.) The exponent's value is equal to the number of zeros in the number expressed in standard notation.

Small numbers can also be expressed in scientific notation but with negative exponents:

Table 3.1.2 shows the powers of 10 with negative exponents. Left side has 10 to a specific power and right side has the equation for the specified power.

10^{-1}	= 0.1 = 1/10
10^{-2}	= 0.01 = 1/100
10^{-3}	= 0.001 = 1/1,000
10^{-4}	= 0.0001 = 1/10,000

and so forth. Again, the value of the exponent is equal to the number of zeros in the denominator of the associated fraction. A negative exponent implies a decimal number less than one.

A number is expressed in scientific notation by writing the first nonzero digit, then a decimal point, and then the rest of the digits. The part of a number in scientific notation that is multiplied by a power of 10 is called the *coefficient*. We determine the power of 10 needed to make that number into the original number and multiply the written number by the proper power of 10. For example, to write 79,345 in scientific notation,

$$79,345 = 7.9345 \times 10,000 = 7.9345 \times 10^4$$

Thus, the number in scientific notation is 7.9345×10^4. For small numbers, the same process is used, but the exponent for the power of 10 is negative:

$$0.000411 = 4.11 \times \frac{1}{10,000} = 4.11 \times 10^{-4}$$

Typically, the extra zero digits at the end or the beginning of a number are not included (Figure $3.1.1$).

Table $3.1.3$ shows examples of measurements in both standard and scientific notation

Measurement	Standard Notation	Scientific Notation
Volume of gas used in the US in 2023	920000000000000 L	9.2×10^{14} L
Diameter of Earth	12800000 L	1.28×10^{7} L
Volume of blood pumped by a human heart in one day	2000 gal	2×10^{3} gal
Mass of a human stirrup bone	0.003 g	3×10^{-3} g
Diameter of a chicken pox virus	0.0000003 m	3×10^{-7} m
Mass of a mycoplasma bacterium	0.0000000000000000001 kg	1×10^{-19} kg

✓ Exercise $3.1.1$

Express these numbers in scientific notation.

a. 306,000
b. 0.00884
c. 2,760,000
d. 0.000000559

Solution

a. The number 306,000 is 3.06 times 100,000, or 3.06 times 10^5. In scientific notation, the number is 3.06 × 10^5.
b. The number 0.00884 is 8.84 times 1/1,000, which is 8.84 times 10^{-3}. In scientific notation, the number is 8.84 × 10^{-3}.
c. The number 2,760,000 is 2.76 times 1,000,000, which is the same as 2.76 times 10^6. In scientific notation, the number is written as 2.76 × 10^6. Note that we omit the zeros at the end of the original number.
d. The number 0.000000559 is 5.59 times 1/10,000,000, which is 5.59 times 10^{-7}. In scientific notation, the number is written as 5.59 × 10^{-7}.

? Exercise $3.1.2$

Express these numbers in scientific notation.

a. 23,070
b. 0.0009706

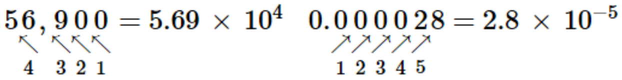
Answer a

2.307 × 10^4

Answer b

9.706 × 10^{-4}

Another way to determine the power of 10 in scientific notation is to count the number of places you need to move the decimal point to get a numerical value between 1 and 10. The number of places equals the power of 10. This number is positive if you move the decimal point to the right and negative if you move the decimal point to the left:



56900 can be written as 5.69 times 10 to the fourth power. 0.000028 can be written as 2.8 times 10 to the negative fifth power.

Many quantities in chemistry are expressed in scientific notation. When performing calculations, you may have to enter a number in scientific notation into a calculator. Be sure you know how to correctly enter a number in scientific notation into your calculator. Different models of calculators require different actions for properly entering scientific notation. If in doubt, consult your instructor immediately.

Units

A number indicates "how much," but the unit indicates "of what." The "of what" is important when communicating a quantity. For example, if you were to ask a friend how close you are to México City and your friend says "six," then your friend isn't giving you complete information. Six *what*? Six miles? Six inches? Six city blocks? The actual distance depends on what units you use.

The official units for chemistry are from the International System of Units, or SI for short. (The letters *SI* stand for the French "le Système International d'unités.") SI specifies certain units for various types of quantities, based on seven fundamental units. These include the **meter** (m), the SI unit of length. It is a little longer than a yard. The SI unit of mass is the **kilogram** (kg), which is about 2.2 pounds (lb). The SI unit of time is the **second** (s). You will need to be familiar with the category of measurement a given unit represents. For example, the gallon is a unit of volume. Table 4 gives examples of different units you may have seen.

Table 3.1.4. Some categories of measurement along with corresponding examples and their unit symbols.

Measurement Type	Examples with their corresponding units
Volume	gallon - g quart - qt liter - L cubic centimeter - cm^3 milliliter - mL
Length/distance	mile - mi meter - m inch - in foot - ft centimeter - cm
Mass (weight)	pound - lb gram - g kilogram - kg
Time	hour - hr minute - min second - s
Temperature	Degrees Farenheit - °F Degrees Celsius - °C Kelvin - K

Key Takeaways

- Standard notation expresses a number normally.
- Scientific notation expresses a number as a coefficient times a power of 10.
- The power of 10 is positive for numbers greater than 1 and negative for numbers between 0 and 1.
- To correctly express a quantity, the measurement value must also have a unit.

- **2.2: Expressing Numbers** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/beginning-chemistry.
- **2.3: Expressing Units** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/beginning-chemistry.

3.2: Significant Figures

Learning Objective

- Understand the purpose behind limiting measured values to a number of significant figures.
- Recognize and record the number of significant figures for a given quantity.
- Limit mathematical results to the proper number of significant figures.

Consider using a ruler to measure the width of an object, as shown in Figure $3.2.1$. The object is definitely more than 1 cm long, so we know with certainty that the first digit in our measurement is 1. We see by counting the tick marks on the ruler that the object is at least three ticks after the 1. If each tick represents 0.1 cm, then we know with certainty that the object is at least 1.3 cm wide. But our ruler does not have any more ticks between the 0.3 and the 0.4 marks, so we can't know exactly how much the next decimal place is. But with a practiced eye we can estimate it. Let us estimate it as about six-tenths of the way between the third and fourth tick marks, which estimates our hundredths place as 6, so we identify a measurement of 1.36 cm for the width of the object. We know the first two digits with certainty but the last digit, the 6, is uncertain.

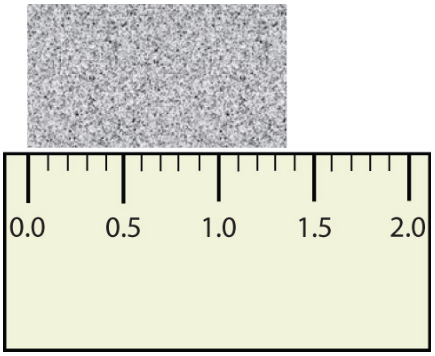


Figure $3.2.1$: Expressing Width. What is the proper way to express the width of this object?

Does it make any sense to try to report a thousandths place for the measurement? No, it doesn't; if we are uncertain about the hundredths place (after all, it was an estimate only), how can we estimate anything beyond that? Our best measurement, then, stops at the hundredths place, and we report 1.36 cm as proper measurement.

If you use a calculator divide two distances, say 3.37 cm by 2.17 cm, you will get the following:

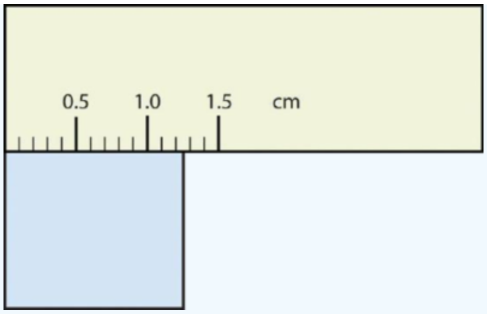
$$3.37 \div 2.17 = 1.5529953917$$

and so on for many more digits. You start with two values that each have three digits, and the answer has *twelve* digits? That does not make much sense, especially if the device used to measure the distances only had marks every 0.1 cm.

The number of digits in a measured value, as well as any results from calculations that use measured values, should always reflect the certainty of the measurement. **Significant figures** (sometimes called significant digits) include all the digits of a measured value that are known with certainty plus one additional digit that is estimated. represent the limits of what values of a measurement or a calculation we know with certainty. This convention enables scientists everywhere to discern the quality and certinty of measured values.

Example $3.2.1$

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

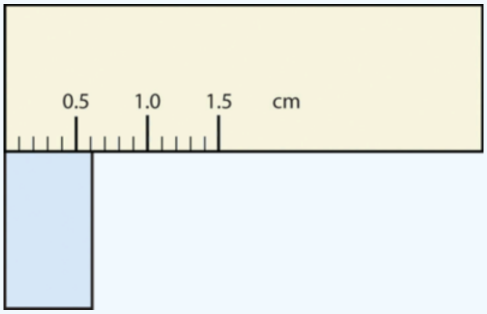


Solution

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

? Exercise 3.2.1

What would be the reported width of this rectangle?



Answer

0.63 cm

In many cases, you will be given a measurement. How can you tell by looking what digits are significant? For example, the reported population of the United States is 306,000,000. Does that mean that it is *exactly* three hundred six million, or is some estimation occurring?

The following conventions dictate which numbers in a reported measurement are significant and which are not significant:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits (i.e., embedded zeros) are significant.
3. Zeros at the end of a number without a decimal point (i.e., trailing zeros) are not significant; they serve only to put the significant digits in the correct positions. However, zeros at the end of any number with a decimal point are significant.
4. Zeros at the beginning of a decimal number (i.e., leading zeros) are not significant; again, they serve only to put the significant digits in the correct positions.

So, by these rules, the population figure of the United States has only three significant figures: the 3, the 6, and the zero between them. The remaining six zeros simply put the 306 in the millions position.

✓ Example 3.2.2

Give the number of significant figures in each measurement.

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

Solution

a. By rule 1, all nonzero digits are significant, so this measurement has three significant figures.
b. By rule 4, the first three zeros are not significant, but by rule 2 the zero between the sixes is; therefore, this number has four significant figures.
c. By rule 2, the two zeros between the twos are significant, so this measurement has four significant figures.
d. The four trailing zeros in the number are not significant, but the other five numbers are, so this number has five significant figures.

? Exercise 3.2.2

Give the number of significant figures in each measurement.

a. 0.000601 m
b. 65.080 kg

Answer a

three significant figures

Answer b

five significant figures

If you use a calculator to evaluate the expression 337/217, you will get the following:

$$337 \div 217 = 1.5529953917$$

and so on for many more digits. Although this answer is correct, it is somewhat presumptuous. You start with two values that each have three digits, and the answer has *twelve* digits? That does not make much sense from a strict numerical point of view.

The rules used to determine the number of digits reported from a calculation depend on what type of calculation is being performed. If the calculation is 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 4.21, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

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

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

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

77.2
10.46
87.66
↑ limit final answer to the tenths column and round up: 87.7

✓ Example 3.2.3

Express the final answer to the proper number of significant figures.

a. 101.2 + 18.702 = ?
b. 202.88 − 1.013 = ?

Solution

a. If we use a calculator to add these two numbers, we would get 119.902. However, most calculators do not understand significant figures, and we need to limit the final answer to the tenths place. Thus, we drop the 02 and report a final answer of 119.9 (rounding down).
b. A calculator would answer 201.867. However, we have to limit our final answer to the hundredths place. Because the first number being dropped is 7, which is greater than 5, we round up and report a final answer of 201.87.

? Exercise 3.2.3

Express the answer for

$$3.445 + 90.83 - 72.4$$

to the proper number of significant figures.

Answer

21.9

If the operations being performed are multiplication or division, the rule is as follows: limit the answer to the number of significant figures that the data value with the *least* number of significant figures has. So if we are dividing 23 by 448, which have two and three significant figures respectively, we should limit the final reported answer to two significant figures (the lesser of two and three significant figures):

$$23 \div 448 = 0.051339286 \approx 0.051$$

The same rounding rules apply in multiplication and division as they do in addition and subtraction.

✓ Example 3.2.4: Significant Figures

Express the final answer to the proper number of significant figures.

a. 76.4 × 180.4 = ?
b. 934.9 ÷ 0.00455 = ?

Solution

a. The first number has three significant figures, while the second number has four significant figures. Therefore, we limit our final answer to three significant figures: 76.4 × 180.4 = 13,782.56 = 13,800.
b. The first number has four significant figures, while the second number has three significant figures. Therefore, we limit our final answer to three significant figures: 934.9 ÷ 0.00455 = 205,472.5275… = 205,000.

? Exercise 3.2.4

Express the final answer to the proper number of significant figures.

a. 22.4 × 8.314 = ?
b. 1.381 ÷ 6.02 = ?

Answer a

186

Answer b

0.229

As you have probably realized by now, the biggest issue in determining the number of significant figures in a value is the zero. Is the zero significant or not? One way to unambiguously determine whether a zero is significant or not is to write a number in scientific notation. Scientific notation will include zeros in the coefficient of the number *only if they are significant*. Thus, the number 8.666×10^6 has four significant figures. However, the number 8.6660×10^6 has five significant figures. That last zero is significant; if it were not, it would not be written in the coefficient. So, when in doubt about expressing the number of significant figures in a quantity, use scientific notation and include the number of zeros that are truly significant.

Summary

- Significant figures in a quantity indicate the number of known values plus one place that is estimated.
- There are rules for which numbers in a quantity are significant and which are not significant.
- In calculations involving addition and subtraction, limit significant figures based on the rightmost place that all values have in common.
- In calculations involving multiplication and division, limit significant figures to the least number of significant figures in all the data values.

3.4: Atomic Mass Unit

What is the mass of an atom?

Masses of individual atoms are very, very small. Using a modern device called a mass spectrometer, it is possible to measure such miniscule masses. An atom of oxygen-16, for example, has a mass of $2.66 \times 10^{-23}\ \mathrm{g}$. While comparisons of masses measured in grams would have some usefulness, it is far more practical to have a system that will allow us to more easily compare relative atomic masses.

Scientists decided on using carbon-12 as the reference standard by which all other masses would be compared. A singe carbon-12 atom has a mass of $1.99 \times 10^{-23}\ \mathrm{g}$. We assigned one atom of carbon-12 a mass of 12 **atomic mass units** (amu). In other words, an atomic mass unit is defined as a mass equal to one twelfth the mass of an atom of carbon-12.

This means

$$1\ \mathrm{amu} = 1.67377 \times 10^{-24}\ \mathrm{g} \tag{3.4.1}$$

This was a somewhat arbitrary decision but it makes writing and reporting the masses of elements a lot easier. As a result of this decision, the masses of all elements are written with more straightforward numbers. For example, one atom of helium-4 has a mass of $4.0026\ \mathrm{amu}$ An atom of sulfur-32 has a mass of $31.972\ \mathrm{amu}$

Key Takeaways

- Carbon-12 is the reference for the atomic mass unit.
- The atomic mass unit simplifies the values written for the masses of atoms and elements

Review

1. What instrument is used to measure the mass of atoms?
2. How much does a single oxygen-16 atom weigh in grams?
3. What is the reference standard for atomic mass units?
4. How is an atomic mass unit defined?
5. Why are the numbers for atomic mass of individual atoms not whole numbers?

3.5: 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 abundances of the isotopes of the element.

Atomic Mass

Since most naturally occurring elements samples are mixtures of isotopes, it is useful to use an average mass of an element. The **atomic mass** of an element is the weighted mass of all the naturally presented isotopes (on earth). To determine the most abundant isotopic form of an element, compare given isotopes to the weighted average on the periodic table. For example, the three hydrogen isotopes in Figure $3.5.2$ are H-1, H-2, and H-3. The atomic mass or weighted average of hydrogen is around 1.008 amu (look again to the periodic table). Of the three hydrogen isotopes, H-1 is closest in mass to the weighted average; therefore, it is the most abundant. The other two isotopes of hydrogen are quite rare, but are very exciting in the world of nuclear science.

You can calculate the atomic mass (or average mass) of an element provided you know the **relative abundances** (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:

$$\text{Atomic mass} = (\%_1)(\text{mass}_1) + (\%_2)(\text{mass}_2) + \cdots \tag{3.5.1}$$

Averages like Equation 1 are known as *weighted averages*. An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes and the masses of those isotopes are known. If all the abundances are not provided, it is safe to assume that all numbers should add up to 100%.

For example, 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 amu. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of 11 amu. How do we calculate the atomic mass of boron?

Boron has two isotopes so we will use the Equation $3.5.1$ and substitute the relative abundances and atomic masses of Boron into Equation $3.5.1$:

$$\begin{aligned}\text{Atomic mass } &= (0.20)(10) + (0.80)(11) \\ &= 10.8\text{ amu}\end{aligned}$$

The mass of an average boron atom, and thus boron's atomic mass, is 10.8 amu

Example $3.5.1$

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 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 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 amu What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

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

Substitute these into the equation, and we get:

$$\begin{aligned}\text{Atomic mass } &= (0.9092)(19.99) + (0.003)(20.99) + (0.0885)(21.99) \\ &= 20.17\text{ amu}\end{aligned}$$

The mass of an average neon atom is 20.17 amu

Exercise 3.5.2

Magnesium has the three isotopes listed in the following table:

Table showing the 3 isotopes of magnesium, the exact mass of each, and the percent abundance of each.

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{24}Mg	23.98504	78.70
^{25}Mg	24.98584	10.13
^{26}Mg	25.98259	11.17

Use these data to calculate the atomic mass of magnesium.

Answer

24.31 amu

Example 3.5.3: 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 amu. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of 11 amu. What is the atomic mass of boron?

Solution

Boron has two isotopes. We will use the equation:

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

- 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:

$$\text{Atomic mass} = \left(0.20\right)\left(10\right) + \left(0.80\right)\left(11\right)$$

$$\text{Atomic mass} = 10.8 \text{ amu}$$

The mass of an average boron atom, and thus boron's atomic mass, is 10.8 amu.

Example 3.5.4: 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 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 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 amu. What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

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

- 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:

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

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

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

The periodic table gives the atomic mass of each element. The atomic mass is a number that usually appears below the element's symbol in each square. Notice that the atomic mass of boron (symbol B) is 10.8, which is what we calculated in Example $3.5.1$, and the atomic mass of neon (symbol Ne) is 20.8, which is what we calculated in Example $3.5.2$. 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 $3.5.5$

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.

3.6: Converting Units

Learning Objective

- Convert from one unit to another unit of the same type.

For calculations in chemistry, we often need to convert from one unit to another. To demonstrate how to do this, let's look at a familiar type of unit conversion, yards to feet. We know that 1 yard (yd) equals 3 feet (ft). To begin, we write this as an equality:

$$1\,yd = 3\,ft$$

Equalities can be re-written as **conversion factors**. Conversion factors are fractions used to change from one unit to another. For example, the equality

$$1\,yd = 3\,ft$$

can be written as:

$$\frac{3\,ft}{1\,yd} \quad \text{OR} \quad \frac{1\,yd}{3\,ft}$$

These factors can be thought of as stating "3 ft per yd," or "1 yd is 3 ft." Every equality can be written as two different conversion factors. Which one you use depends on the unit of the starting value.

Converting yards to feet

If you want to know how many feet are in four yards, you may be able to quickly determine the answer in your head. If there are three feet in one yard, there would be 12 feet in four yards. Sometimes a conversion is not easy to do in your head. The following method can be used to solve any type of conversion problem. Because we want to convert yards to feet, we want the unit of yards to go away or cancel. To do this the strategy is to multiply by the conversion factor that will cancel the unit you do not want:

$$4\,yd \times \frac{3\,ft}{1\,yd}$$

We are essentially multiplying fractions where you multiply all the numerators and denominators across. If it helps, you can write or imagine the 3yd term as a fraction with a 1 on the bottom. Remember that if the same thing appears in the numerator and denominator of a fraction, they cancel. In this case, what cancels is the unit *yard*:

$$\frac{4\ \cancel{yd} \times 3\,ft}{1\ \cancel{yd}} = \frac{4 \times 3\,ft}{1} = 12\,ft$$

You can see we get the same answer as before, but in this case, we used a more formal procedure that can be applied to a variety of problems.

Converting feet to yards

If we had wanted to determine the number of yards in a given number of feet, we would choose the other conversion factor from the equality. For example, to calculate the number of yards in 42 feet, multiply 42 ft by the conversion factor 1yd per 3ft:

$$42\,ft \times \frac{1\,yd}{3\,ft}$$

Which becomes:

$$42\ \cancel{ft} \times \frac{1\,yd}{3\ \cancel{ft}} = 14\,yd$$

The ability to construct and apply proper conversion factors is a very powerful mathematical technique in chemistry. In addition to using it to convert units, it is the foundation of further calculations to determine quantities in chemical reactions.

✓ Example 3.6.1

a. Convert 35.9 kL to liters.
b. Convert 555 nm to meters.

Solution

a. We will use the fact that 1 kL = 1,000 L. Of the two conversion factors that can be defined, the one that will work is 1000L/1kL. Applying this conversion factor, we get:

$$35.9\,kL \times \frac{1000\,L}{1\,kL} = 35,900\,L$$

b. We will use the fact that 1 nm = 1/1,000,000,000 m, which we will rewrite as 1,000,000,000 nm = 1 m, or 10^9 nm = 1 m. Of the two possible conversion factors, the appropriate one has the nm unit in the denominator:

$$\frac{1\,m}{10^9\,nm}$$

Applying this conversion factor, we get:

$$555\,nm \times \frac{1m}{10^9 nm} = 0.000000555\,m = 5.55 \times 10^{-7}\,m$$

In the final step, we expressed the answer in scientific notation.

? Exercise 3.6.2

a. Convert 67.08 μL to liters.
b. Convert 56.8 m to kilometers.

Answer a

6.708×10^{-5} L

Answer b

5.68×10^{-2} km

What if we have a derived unit that is the product of more than one unit, such as m^2? Suppose we want to convert square meters to square centimeters? The key is to remember that m^2 means m × m, which means we have *two* meter units in our derived unit. That means we have to include *two* conversion factors, one for each unit. For example, to convert 17.6 m^2 to square centimeters, we perform the conversion as follows:

$$\begin{aligned} 17.6m^2 &= 17.6(m \times m) \times \frac{100cm}{1m} \times \frac{100cm}{1m} \\ &= 176000\,cm \times cm \\ &= 1.76 \times 10^5\,cm^2 \end{aligned} \tag{3.6.1}$$

✓ Example 3.6.3

How many cubic centimeters are in 0.883 m^3?

Solution

With an exponent of 3, we have three length units, so by extension we need to use three conversion factors between meters and centimeters. Thus, we have:

$$0.883m^3 \times \frac{100\,cm}{1\,m} \times \frac{100\,cm}{1\,m} \times \frac{100\,cm}{1\,m} = 883000\,cm^3 = 8.83 \times 10^5\,cm^3$$

You should demonstrate to yourself that the three meter units do indeed cancel.

When considering the significant figures of a final numerical answer in a conversion, there is one important case where a number does not impact the number of significant figures in a final answer: the so-called **exact number**. An exact number is a number from a defined relationship, not a measured one. For example, the prefix *kilo*- means 1,000-*exactly* 1,000, no more or no less. Thus, in constructing the conversion factor:

$$\frac{1000\,g}{1\,kg}$$

neither the 1,000 nor the 1 enter into our consideration of significant figures. The numbers in the numerator and denominator are defined exactly by what the prefix *kilo*- means. Another way of thinking about it is that these numbers can be thought of as having an infinite number of significant figures, such as:

$$\frac{1000.0000000000\ldots\ g}{1.0000000000\ldots\ kg}$$

The other numbers in the calculation will determine the number of significant figures in the final answer.

Key Takeaways

- Units can be converted to other units using the proper conversion factors.
- Conversion factors are constructed from equalities that relate two different units.
- Unit conversion is a powerful mathematical technique in chemistry that must be mastered.
- Exact numbers do not affect the determination of significant figures.

3.7: Other Units - Temperature and Density

Learning Objective

- Learn about the various temperature scales that are commonly used in chemistry.
- Define density and use it as a conversion factor.

There are other units in chemistry that are important, and we will cover others over the course of the entire book. One of the fundamental quantities in science is temperature. Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees, and there are several temperature scales in use. In the United States, the commonly used temperature scale is the *Fahrenheit scale* (symbolized by °F and spoken as "degrees Fahrenheit"). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32°F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212°F.

Science also uses other scales to express temperature. The Celsius scale (symbolized by °C and spoken as "degrees Celsius") is a temperature scale where 0°C is the freezing point of water and 100°C is the boiling point of water; the scale is divided into 100 divisions between these two landmarks and extended higher and lower. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}\mathrm{C} = (^{\circ}\mathrm{F} - 32) \times \tfrac{5}{9} \tag{3.7.1}$$

$$^{\circ}\mathrm{F} = \left(^{\circ}\mathrm{C} \times \tfrac{9}{5}\right) + 32 \tag{3.7.2}$$

Example 3.7.1: Conversions

a. What is 98.6 °F in degrees Celsius?
b. What is 25.0 °C in degrees Fahrenheit?

Solution

a. Using Equation 3.7.1, we have

$$\begin{aligned} ^{\circ}C &= (98.6 - 32) \times \frac{5}{9} \\ &= 66.6 \times \frac{5}{9} \\ &= 37.0^{\circ}C \end{aligned}$$

b. Using Equation 3.7.2, we have

$$\begin{aligned} ^{\circ}F &= \left(25.0 \times \frac{9}{5}\right) + 32 \\ &= 45.0 + 32 \\ &= 77.0^{\circ}F \end{aligned}$$

Exercise 3.7.1

a. Convert 0 °F to degrees Celsius.
b. Convert 212 °C to degrees Fahrenheit.

Answer a

−17.8 °C

Answer b

414 °F

The fundamental unit of temperature (another fundamental unit of science, bringing us to four) in SI is the kelvin (K). The Kelvin temperature scale (note that the name of the scale capitalizes the word *Kelvin*, but the unit itself is lowercase) uses degrees that are the same size as the Celsius degree, but the numerical scale is shifted up by 273.15 units. That is, the conversion between the Kelvin and Celsius scales is as follows:

$$K = {}^{\circ}C + 273.15$$

For most purposes, it is acceptable to use 273 instead of 273.15. Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as "two hundred ninety-five kelvins" and not "two hundred ninety-five degrees Kelvin."

The reason that the Kelvin scale is defined this way is because there exists a minimum possible temperature called absolute zero (zero kelvins). The Kelvin temperature scale is set so that 0 K is absolute zero, and temperature is counted upward from there. Normal room temperature is about 295 K, as seen in the following example.

✓ Example 3.7.2: Room Temperature

If normal room temperature is 72.0°F, what is room temperature in degrees Celsius and kelvin?

Solution

First, we use the formula to determine the temperature in degrees Celsius:

$$\begin{aligned} {}^{\circ}C &= (72.0 - 32) \times \frac{5}{9} \\ &= 40.0 \times \frac{5}{9} \\ &= 22.2^{\circ}C \end{aligned}$$

Then we use the appropriate formula above to determine the temperature in the Kelvin scale:

$$\begin{aligned} K &= 22.2^{\circ}C + 273.15 \\ &= 295.4K \end{aligned}$$

So, room temperature is about 295 K.

? Exercise 3.7.2

What is 98.6°F on the Kelvin scale?

Answer

310.2 K

Figure 3.7.1 compares the three temperature scales. Note that science uses the Celsius and Kelvin scales almost exclusively; virtually no practicing chemist expresses laboratory-measured temperatures with the Fahrenheit scale. In fact, the United States is one of the few countries in the world that still uses the Fahrenheit scale on a daily basis. The other two countries are Liberia and Myanmar (formerly Burma). People driving near the borders of Canada or Mexico may pick up local radio stations on the other side of the border that express the daily weather in degrees Celsius, so do not get confused by their weather reports.

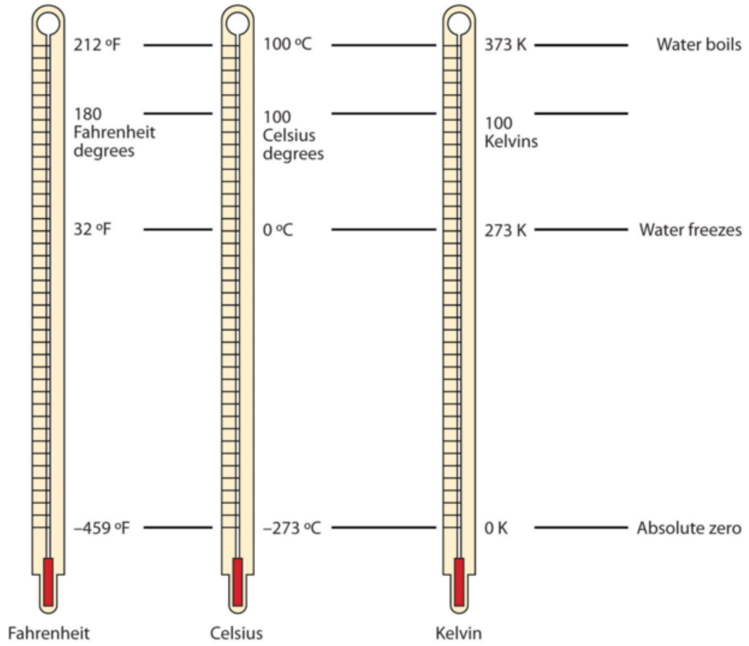


Figure $3.7.1$: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales.

Density

Density is a physical property that is defined as a substance's mass divided by its volume:

$$density = \frac{mass}{volume} \Rightarrow d = \frac{m}{v}$$

Density is usually a measured property of a substance, so its numerical value affects the significant figures in a calculation. Notice that density is defined in terms of two dissimilar units, mass and volume. That means that density overall has derived units, just like velocity. Common units for density include g/mL, g/cm^3, g/L, kg/L, and even kg/m^3. Densities for some common substances are listed in Table $3.7.1$.

Table $3.7.1$: Densities of Some Common Substances

Substance	**Density (g/mL or g/cm^3)**
water	1.0
gold	19.3
mercury	13.6
air	0.0012
cork	0.22–0.26
aluminum	2.7
iron	7.87

Because of how it is defined, density can act as a conversion factor for switching between units of mass and volume. For example, suppose you have a sample of aluminum that has a volume of 7.88 cm^3. How can you determine what mass of aluminum you have without measuring it? You can use the volume to calculate it. If you multiply the given volume by the known density (from Table $3.7.1$), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

$$7.88\ \cancel{cm^3} \times \frac{2.7\ g}{\cancel{cm^3}} = 21\ g \text{ of aluminium}$$

where we have limited our answer to two significant figures.

✓ Example 3.7.3: Mercury

What is the mass of 44.6 mL of mercury?

Solution

Use the density from Table 3.7.1 "Densities of Some Common Substances" as a conversion factor to go from volume to mass:

$$44.6\ \cancel{mL} \times \frac{13.6\,g}{\cancel{mL}} = 607\,g$$

The mass of the mercury is 607 g.

? Exercise 3.7.3

What is the mass of 25.0 cm^3 of iron?

Answer

197 g

Density can also be used as a conversion factor to convert mass to volume—but care must be taken. We have already demonstrated that the number that goes with density normally goes in the numerator when density is written as a fraction. Take the density of gold, for example:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

Although this was not previously pointed out, it can be assumed that there is a 1 in the denominator:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

That is, the density value tells us that we have 19.3 grams for every 1 milliliter of volume, and the 1 is an exact number. When we want to use density to convert from mass to volume, the numerator and denominator of density need to be switched—that is, we must take the *reciprocal* of the density. In so doing, we move not only the units, but also the numbers:

$$\frac{1}{d} = \frac{1\,mL}{19.3\,g}$$

This reciprocal density is still a useful conversion factor, but now the mass unit will cancel and the volume unit will be introduced. Thus, if we want to know the volume of 45.9 g of gold, we would set up the conversion as follows:

$$45.9\ \cancel{g} \times \frac{1\,mL}{19.3\ \cancel{g}} = 2.38\,mL$$

Note how the mass units cancel, leaving the volume unit, which is what we are looking for.

✓ Example 3.7.4: Calculating Volume from Density

A cork stopper from a bottle of wine has a mass of 3.78 g. If the density of cork is 0.22 g/cm^3, what is the volume of the cork?

Solution

To use density as a conversion factor, we need to take the reciprocal so that the mass unit of density is in the denominator. Taking the reciprocal, we find:

$$\frac{1}{d} = \frac{1\,cm^3}{0.22\,g}$$

We can use this expression as the conversion factor. So

$$3.78\ \cancel{g} \times \frac{1\ cm^3}{0.22\ \cancel{g}} = 17.2\ cm^3$$

Exercise 3.7.4

What is the volume of 3.78 g of gold?

Answer

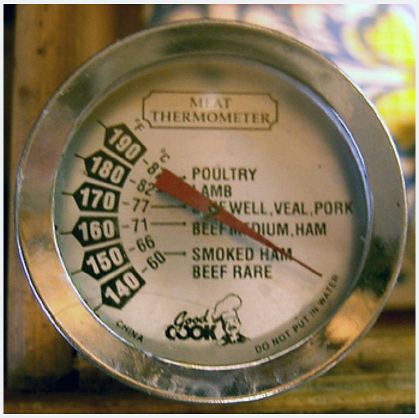
0.196 cm^3

Care must be used with density as a conversion factor. Make sure the mass units are the same, or the volume units are the same, before using density to convert to a different unit. Often, the unit of the given quantity must be first converted to the appropriate unit before applying density as a conversion factor.

Food and Drink Application: Cooking Temperatures

Because degrees Fahrenheit is the common temperature scale in the United States, kitchen appliances, such as ovens, are calibrated in that scale. A cool oven may be only 150°F, while a cake may be baked at 350°F and a chicken roasted at 400°F. The broil setting on many ovens is 500°F, which is typically the highest temperature setting on a household oven.

People who live at high altitudes, typically 2,000 ft above sea level or higher, are sometimes urged to use slightly different cooking instructions on some products, such as cakes and bread, because water boils at a lower temperature the higher in altitude you go, meaning that foods cook slower. For example, in Cleveland water typically boils at 212°F (100°C), but in Denver, the Mile-High City, water boils at about 200°F (93.3°C), which can significantly lengthen cooking times. Good cooks need to be aware of this.



A meat thermometer with a dial. Notice the markings for Fahrenheit (outer scale) and Celsius (inner scale) temperatures. Recipes for cooking food in an oven can use very different numbers, depending on the country you're in. (CC BY2.0 Bev Sykes)

At the other end is pressure cooking. A pressure cooker is a closed vessel that allows steam to build up additional pressure, which increases the temperature at which water boils. A good pressure cooker can get to temperatures as high as 252°F (122°C); at these temperatures, food cooks much faster than it normally would. Great care must be used with pressure cookers because of the high pressure and high temperature. (When a pressure cooker is used to sterilize medical instruments, it is called an *autoclave*.)

Other countries use the Celsius scale for everyday purposes. Therefore, oven dials in their kitchens are marked in degrees Celsius. It can be confusing for US cooks to use ovens abroad—a 425°F oven in the United States is equivalent to a 220°C oven in other countries. These days, many oven thermometers are marked with both temperature scales.

Key Takeaways

- Chemistry uses the Celsius and Kelvin scales to express temperatures.
- A temperature on the Kelvin scale is the Celsius temperature plus 273.15.
- The minimum possible temperature is absolute zero and is assigned 0 K on the Kelvin scale.
- Density relates the mass and volume of a substance.
- Density can be used to calculate volume from a given mass or mass from a given volume.

3.E: Measurements (Exercises)

Exercises (Expressing Numbers)

1. Express these numbers in scientific notation.

    a. 56.9
    b. 563,100
    c. 0.0804
    d. 0.00000667

2. Express these numbers in scientific notation.

    a. −890,000
    b. 602,000,000,000
    c. 0.0000004099
    d. 0.0000000000000011

3. Express these numbers in scientific notation.

    a. 0.00656
    b. 65,600
    c. 4,567,000
    d. 0.000005507

4. Express these numbers in scientific notation.

    a. 65
    b. −321.09
    c. 0.000077099
    d. 0.000000000218

5. Express these numbers in standard notation.

    a. 1.381×10^{5}
    b. 5.22×10^{-7}
    c. 9.998×10^{4}

6. Express these numbers in standard notation.

    a. 7.11×10^{-2}
    b. 9.18×10^{2}
    c. 3.09×10^{-10}

7. Express these numbers in standard notation.

    a. 8.09×10^{0}
    b. 3.088×10^{-5}
    c. -4.239×10^{2}

8. Express these numbers in standard notation.

    a. 2.87×10^{-8}
    b. 1.78×10^{11}
    c. 1.381×10^{-23}

9. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

    a. 72.44×10^{3}
    b. $9{,}943 \times 10^{-5}$
    c. $588{,}399 \times 10^{2}$

10. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

   a. 0.000077×10^{-7}
   b. 0.000111×10^{8}
   c. $602{,}000 \times 10^{18}$

11. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.
    a. 345.1×10^{2}
    b. 0.234×10^{-3}
    c. $1{,}800 \times 10^{-2}$

12. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.
    a. $8{,}099 \times 10^{-8}$
    b. 34.5×10^{0}
    c. 0.000332×10^{4}

13. Write these numbers in scientific notation by counting the number of places the decimal point is moved.
    a. 123,456.78
    b. 98,490
    c. 0.000000445

14. Write these numbers in scientific notation by counting the number of places the decimal point is moved.
    a. 0.000552
    b. 1,987
    c. 0.00000000887

15. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $456 \times (7.4 \times 10^{8}) = ?$
    b. $(3.02 \times 10^{5}) \div (9.04 \times 10^{15}) = ?$
    c. $0.0044 \times 0.000833 = ?$

16. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $98{,}000 \times 23{,}000 = ?$
    b. $98{,}000 \div 23{,}000 = ?$
    c. $(4.6 \times 10^{-5}) \times (2.09 \times 10^{3}) = ?$

17. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $45 \times 132 \div 882 = ?$
    b. $[(6.37 \times 10^{4}) \times (8.44 \times 10^{-4})] \div (3.2209 \times 10^{15}) = ?$

18. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $(9.09 \times 10^{8}) \div [(6.33 \times 10^{9}) \times (4.066 \times 10^{-7})] = ?$
    b. $9{,}345 \times 34.866 \div 0.00665 = ?$

Answers

1. a. 5.69×10^{1}
   b. 5.631×10^{5}
   c. 8.04×10^{-2}
   d. 6.67×10^{-6}

3. a. 6.56×10^{-3}
   b. 6.56×10^{4}
   c. 4.567×10^{6}
   d. 5.507×10^{-6}

5. a. 138,100
   b. 0.000000522
   c. 99,980

7. a. 8.09
   b. 0.00003088
   c. −423.9
9. a. 7.244×10^4
   b. 9.943×10^{-2}
   c. 5.88399×10^7
11. a. 3.451×10^4
    b. 2.34×10^{-4}
    c. 1.8×10^1
13. a. 1.2345678×10^5
    b. 9.849×10^4
    c. 4.45×10^{-7}
15. a. 3.3744×10^{11}
    b. 3.3407×10^{-11}
    c. 3.665×10^{-6}
17. a. 6.7346×10^0
    b. 1.6691×10^{-14}

Exercises (Expressing Units)

1. Identify the unit in each quantity.

   a. 2 boxes of crayons
   b. 3.5 grams of gold

2. Identify the unit in each quantity.

   a. 32 oz of cheddar cheese
   b. 0.045 cm^3 of water

3. Identify the unit in each quantity.

   a. 9.58 s (the current world record in the 100 m dash)
   b. 6.14 m (the current world record in the pole vault)

4. Identify the unit in each quantity.

   a. 2 dozen eggs
   b. 2.4 km/s (the escape velocity of the moon, which is the velocity you need at the surface to escape the moon's gravity)

5. Indicate what multiplier each prefix represents.

   a. k
   b. m
   c. M

6. Indicate what multiplier each prefix represents.

   a. c
   b. G
   c. μ

7. Give the prefix that represents each multiplier.

   a. 1/1,000th ×
   b. 1,000 ×
   c. 1,000,000,000 ×

8. Give the prefix that represents each multiplier.

   a. 1/1,000,000,000th ×

b. 1/100th ×
c. 1,000,000 ×

9. Complete the following table with the missing information.

Table with Units on the right and Abbreviation on the left side. Missing units on the second and third rows on the right side of the table. Missing abbreviations on the first and fourth rows on the left side of the table.

Unit	Abbreviation
kilosecond	
	mL
	Mg
centimeter	

10. Complete the following table with the missing information.

Table with Units on the right and Abbreviation on the left side. Missing units on the third and fourth rows on the right side of the table. Missing abbreviations on the first, second, and fifth row on the left side of the table.

Unit	Abbreviation
kilometer per second	
second	
	cm^3
	µL
nanosecond	

11. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

a. 3.44×10^{-6} s
b. 3,500 L
c. 0.045 m

12. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

a. 0.000066 m/s (Hint: you need consider only the unit in the numerator.)
b. 4.66×10^{6} s
c. 7,654 L

13. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

a. 43,600 mL
b. 0.0000044 m
c. 1,438 ms

14. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

a. 0.000000345 m^3
b. 47,000,000 mm^3
c. 0.00665 L

15. Multiplicative prefixes are used for other units as well, such as computer memory. The basic unit of computer memory is the byte (b). What is the unit for one million bytes?

16. You may have heard the terms *microscale* or *nanoscale* to represent the sizes of small objects. What units of length do you think are useful at these scales? What fractions of the fundamental unit of length are these units?

17. Acceleration is defined as a change in velocity per time. Propose a unit for acceleration in terms of the fundamental SI units.

18. Density is defined as the mass of an object divided by its volume. Propose a unit of density in terms of the fundamental SI units.

Answers

1.
    a. boxes of crayons
    b. grams of gold

3.
    a. seconds
    b. meters

5.
    a. 1,000 x
    b. 1/1,000 x
    c. 1,000,000 x

7.
    a. milli-
    b. kilo-
    c. giga-

9.

Table with Units on the right and Abbreviation on the left side.

Unit	Abbreviation
kilosecond	ks
milliliter	mL
megagram	Mg
centimeter	cm

11.
    a. 3.44 µs
    b. 3.5 kL
    c. 4.5 cm

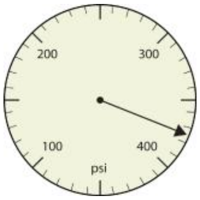
13.
    a. 43.6 mL
    b. 4.4 µm
    c. 1.438 s

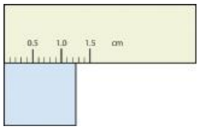
15. megabytes (Mb)

17. meters/second^2

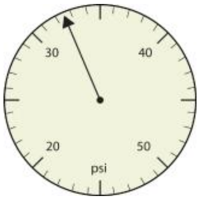
Exercises (Significant Figures)

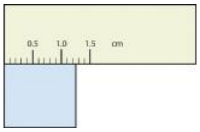
1. Express each measurement to the correct number of significant figures.





2. Express each measurement to the correct number of significant figures.





3. How many significant figures do these numbers have?

   a. 23
   b. 23.0
   c. 0.00023
   d. 0.0002302

4. How many significant figures do these numbers have?

   a. 5.44×10^{8}
   b. 1.008×10^{-5}
   c. 43.09
   d. 0.0000001381

5. How many significant figures do these numbers have?

   a. 765,890
   b. 765,890.0
   c. 1.2000×10^{5}
   d. 0.0005060

6. How many significant figures do these numbers have?

   a. 0.009
   b. 0.0000009
   c. 65,444
   d. 65,040

7. Compute and express each answer with the proper number of significant figures, rounding as necessary.

   a. 56.0 + 3.44 = ?
   b. 0.00665 + 1.004 = ?
   c. 45.99 − 32.8 = ?
   d. 45.99 − 32.8 + 75.02 = ?

8. Compute and express each answer with the proper number of significant figures, rounding as necessary.

   1. 1.005 + 17.88 = ?
   2. 56,700 − 324 = ?
   3. 405,007 − 123.3 = ?
   4. 55.5 + 66.66 − 77.777 = ?

9. Compute and express each answer with the proper number of significant figures, rounding as necessary.

a. 56.7 × 66.99 = ?
b. 1.0÷ 77 = ?
c. 1.00÷ 77.0 = ?
d. 6.022 × 1.89 = ?

10. Compute and express each answer with the proper number of significant figures, rounding as necessary.

a. 0.000440 × 17.22 = ?
b. 203,000 ÷ 0.044 = ?
c. 67 × 85.0 × 0.0028 = ?
d. 999,999 ÷ 3,310 = ?

11. a. Write the number 87,449 in scientific notation with four significant figures.
b. Write the number 0.000066600 in scientific notation with five significant figures.

12. a. Write the number 306,000,000 in scientific notation to the proper number of significant figures.
b. Write the number 0.0000558 in scientific notation with two significant figures

13. Perform each calculation and limit each answer to three significant figures.

a. 67,883 × 0.004321 = ?
b. (9.67 × 10^3) × 0.0055087 = ?

14. Perform each calculation and limit each answer to four significant figures.

a. 18,900 × 76.33 ÷ 0.00336 = ?
b. 0.77604 ÷ 76,003 × 8.888 = ?

Answers

1.

a. 375 psi
b. 1.30 cm

3.

a. two
b. three
c. two
d. four

5.

a. five
b. seven
c. five
d. four

7.

a. 59.4
b. 1.011
c. 13.2
d. 88.2

9.

a. 3.80 × 10^3
b. 0.013
c. 0.0130
d. 11.4

11. a. 8.745×10^4
b. 6.6600×10^{-5}

13. a. 293
    b. 53.3

Exercises (Converting Units)

1. Write the two conversion factors that exist between the two given units.

   a. milliliters and liters
   b. microseconds and seconds
   c. kilometers and meters

2. Write the two conversion factors that exist between the two given units.

   a. kilograms and grams
   b. milliseconds and seconds
   c. centimeters and meters

3. Perform the following conversions.

   a. 5.4 km to meters
   b. 0.665 m to millimeters
   c. 0.665 m to kilometers

4. Perform the following conversions.

   a. 90.6 mL to liters
   b. 0.00066 ML to liters
   c. 750 L to kiloliters

5. Perform the following conversions.

   a. 17.8 μg to grams
   b. 7.22×10^2 kg to grams
   c. 0.00118 g to nanograms

6. Perform the following conversions.

   a. 833 ns to seconds
   b. 5.809 s to milliseconds
   c. 2.77×10^6 s to megaseconds

7. Perform the following conversions.

   a. 9.44 m^2 to square centimeters
   b. 3.44×10^8 mm^3 to cubic meters

8. Perform the following conversions.

   a. 0.00444 cm^3 to cubic meters
   b. 8.11×10^2 m^2 to square nanometers

9. Why would it be inappropriate to convert square centimeters to cubic meters?

10. Why would it be inappropriate to convert from cubic meters to cubic seconds?

11. Perform the following conversions.

    a. 45.0 m/min to meters/second
    b. 0.000444 m/s to micrometers/second
    c. 60.0 km/h to kilometers/second

12. Perform the following conversions.

    a. 3.4×10^2 cm/s to centimeters/minute
    b. 26.6 mm/s to millimeters/hour
    c. 13.7 kg/L to kilograms/milliliters

13. Perform the following conversions.

- a. 0.674 kL to milliliters
- b. 2.81 × 10^{12} mm to kilometers
- c. 94.5 kg to milligrams

14. Perform the following conversions.

- a. 6.79 × 10^{-6} kg to micrograms
- b. 1.22 mL to kiloliters
- c. 9.508 × 10^{-9} ks to milliseconds

15. Perform the following conversions.

- a. 6.77 × 10^{14} ms to kiloseconds
- b. 34,550,000 cm to kilometers

16. Perform the following conversions.

- a. 4.701 × 10^{15} mL to kiloliters
- b. 8.022 × 10^{-11} ks to microseconds

17. Perform the following conversions. Note that you will have to convert units in both the numerator and the denominator.

- a. 88 ft/s to miles/hour (Hint: use 5,280 ft = 1 mi.)
- b. 0.00667 km/h to meters/second

18. Perform the following conversions. Note that you will have to convert units in both the numerator and the denominator.

- a. 3.88 × 10^{2} mm/s to kilometers/hour
- b. 1.004 kg/L to grams/milliliter

19. What is the area in square millimeters of a rectangle whose sides are 2.44 cm × 6.077 cm? Express the answer to the proper number of significant figures.

20. What is the volume in cubic centimeters of a cube with sides of 0.774 m? Express the answer to the proper number of significant figures.

21. The formula for the area of a triangle is 1/2 × base × height. What is the area of a triangle in square centimeters if its base is 1.007 m and its height is 0.665 m? Express the answer to the proper number of significant figures.

22. The formula for the area of a triangle is 1/2 × base × height. What is the area of a triangle in square meters if its base is 166 mm and its height is 930.0 mm? Express the answer to the proper number of significant figures.

Answers

1.

a. $\frac{1000 mL}{1 L} \; and \; \frac{1 L}{1000 mL}$

b. $\frac{1000000 \mu s}{1 s} \; and \; \frac{1 s}{1000000 \mu s}$

c. $\frac{1000 m}{1 km} \; and \; \frac{1 km}{1000 m}$

3.

- a. 5,400 m
- b. 665 mm
- c. 6.65 × 10^{-4} km

5.

- a. 1.78 × 10^{-5} g
- b. 7.22 × 10^{5} g

c. 1.18×10^6 ng

7.

a. 94,400 cm^2
b. 0.344 m^3

9. One is a unit of area, and the other is a unit of volume.

11.

a. 0.75 m/s
b. 444 µm/s
c. 1.666×10^{-2} km/s

13.

a. 674,000 mL
b. 2.81×10^6 km
c. 9.45×10^7 mg

15.

a. 6.77×10^8 ks
b. 345.5 km

17.

a. 6.0×10^1 mi/h
b. 0.00185 m/s

19. 1.48×10^3 mm^2

21. 3.35×10^3 cm^2

Exercises (Other Units - Temperature and Density)

1. Perform the following conversions.

a. 255°F to degrees Celsius
b. −255°F to degrees Celsius
c. 50.0°C to degrees Fahrenheit
d. −50.0°C to degrees Fahrenheit

2. Perform the following conversions.

a. 1,065°C to degrees Fahrenheit
b. −222°C to degrees Fahrenheit
c. 400.0°F to degrees Celsius
d. 200.0°F to degrees Celsius

3. Perform the following conversions.

a. 100.0°C to kelvins
b. −100.0°C to kelvins
c. 100 K to degrees Celsius
d. 300 K to degrees Celsius

4. Perform the following conversions.

a. 1,000.0 K to degrees Celsius
b. 50.0 K to degrees Celsius
c. 37.0°C to kelvins
d. −37.0°C to kelvins

5. Convert 0 K to degrees Celsius. What is the significance of the temperature in degrees Celsius?
6. Convert 0 K to degrees Fahrenheit. What is the significance of the temperature in degrees Fahrenheit?
7. The hottest temperature ever recorded on the surface of the earth was 136°F in Libya in 1922. What is the temperature in degrees Celsius and in kelvins?
8. The coldest temperature ever recorded on the surface of the earth was −128.6°F in Vostok, Antarctica, in 1983. What is the temperature in degrees Celsius and in kelvins?
9. Give at least three possible units for density.
10. What are the units when density is inverted? Give three examples.
11. A sample of iron has a volume of 48.2 cm^3. What is its mass?
12. A sample of air has a volume of 1,015 mL. What is its mass?
13. The volume of hydrogen used by the *Hindenburg*, the German airship that exploded in New Jersey in 1937, was 2.000×10^8 L. If hydrogen gas has a density of 0.0899 g/L, what mass of hydrogen was used by the airship?
14. The volume of an Olympic-sized swimming pool is $2.50 \times 10^9\ \text{cm}^3$. If the pool is filled with alcohol ($d = 0.789\ \text{g/cm}^3$), what mass of alcohol is in the pool?
15. A typical engagement ring has 0.77 cm^3 of gold. What mass of gold is present?
16. A typical mercury thermometer has 0.039 mL of mercury in it. What mass of mercury is in the thermometer?
17. What is the volume of 100.0 g of lead if lead has a density of 11.34 g/cm^3?
18. What is the volume of 255.0 g of uranium if uranium has a density of 19.05 g/cm^3?
19. What is the volume in liters of 222 g of neon if neon has a density of 0.900 g/L?
20. What is the volume in liters of 20.5 g of sulfur hexafluoride if sulfur hexafluoride has a density of 6.164 g/L?
21. Which has the greater volume, 100.0 g of iron ($d = 7.87\ \text{g/cm}^3$) or 75.0 g of gold ($d = 19.3\ \text{g/cm}^3$)?
22. Which has the greater volume, 100.0 g of hydrogen gas ($d = 0.0000899\ \text{g/cm}^3$) or 25.0 g of argon gas ($d = 0.00178\ \text{g/cm}^3$)?

Answers

1.
    a. 124°C
    b. −159°C
    c. 122°F
    d. −58°F

3.
    a. 373 K
    b. 173 K
    c. −173°C
    d. 27°C

5. −273°C. This is the lowest possible temperature in degrees Celsius.

7. 57.8°C; 331 K

9. g/mL, g/L, and kg/L (answers will vary)

11. 379 g

13. 1.80×10^7 g

15. 15 g

17. 8.818 cm^3

19. 247 L

21. The 100.0 g of iron has the greater volume

Additional Exercises

1. Evaluate 0.00000000552 × 0.0000000006188 and express the answer in scientific notation. You may have to rewrite the original numbers in scientific notation first.

2. Evaluate 333,999,500,000 ÷ 0.00000000003396 and express the answer in scientific notation. You may need to rewrite the original numbers in scientific notation first.

3. Express the number 6.022×10^{23} in standard notation.

4. Express the number 6.626×10^{-34} in standard notation.

5. When powers of 10 are multiplied together, the powers are added together. For example, $10^2 \times 10^3 = 10^{2+3} = 10^5$. With this in mind, can you evaluate $(4.506 \times 10^4) \times (1.003 \times 10^2)$ without entering scientific notation into your calculator?

6. When powers of 10 are divided into each other, the bottom exponent is subtracted from the top exponent. For example, $10^5/10^3 = 10^{5-3} = 10^2$. With this in mind, can you evaluate $(8.552 \times 10^6) \div (3.129 \times 10^3)$ without entering scientific notation into your calculator?

7. Consider the quantity two dozen eggs. Is the number in this quantity "two" or "two dozen"? Justify your choice.

8. Consider the quantity two dozen eggs. Is the unit in this quantity "eggs" or "dozen eggs"? Justify your choice.

9. Fill in the blank: 1 km = ______________ µm.

10. Fill in the blank: 1 Ms = ______________ ns.

11. Fill in the blank: 1 cL = ______________ ML.

12. Fill in the blank: 1 mg = ______________ kg.

13. Express 67.3 km/h in meters/second.

14. Express 0.00444 m/s in kilometers/hour.

15. Using the idea that 1.602 km = 1.000 mi, convert a speed of 60.0 mi/h into kilometers/hour.

16. Using the idea that 1.602 km = 1.000 mi, convert a speed of 60.0 km/h into miles/hour.

17. Convert 52.09 km/h into meters/second.

18. Convert 2.155 m/s into kilometers/hour.

19. Use the formulas for converting degrees Fahrenheit into degrees Celsius to determine the relative size of the Fahrenheit degree over the Celsius degree.

20. Use the formulas for converting degrees Celsius into kelvins to determine the relative size of the Celsius degree over kelvins.

21. What is the mass of 12.67 L of mercury?

22. What is the mass of 0.663 m^3 of air?

23. What is the volume of 2.884 kg of gold?

24. What is the volume of 40.99 kg of cork? Assume a density of 0.22 g/cm^3.

Answers

1. 3.42×10^{-18}

3. 602,200,000,000,000,000,000,000

5. 4.520×10^6

7. The quantity is two; dozen is the unit.

9.1,000,000,000

11. 1/100,000,000

13. 18.7 m/s

15. 96.1 km/h

17. 14.47 m/s

19. One Fahrenheit degree is nine-fifths the size of a Celsius degree.

21. 1.72×10^5 g

23. 149 mL

CHAPTER OVERVIEW

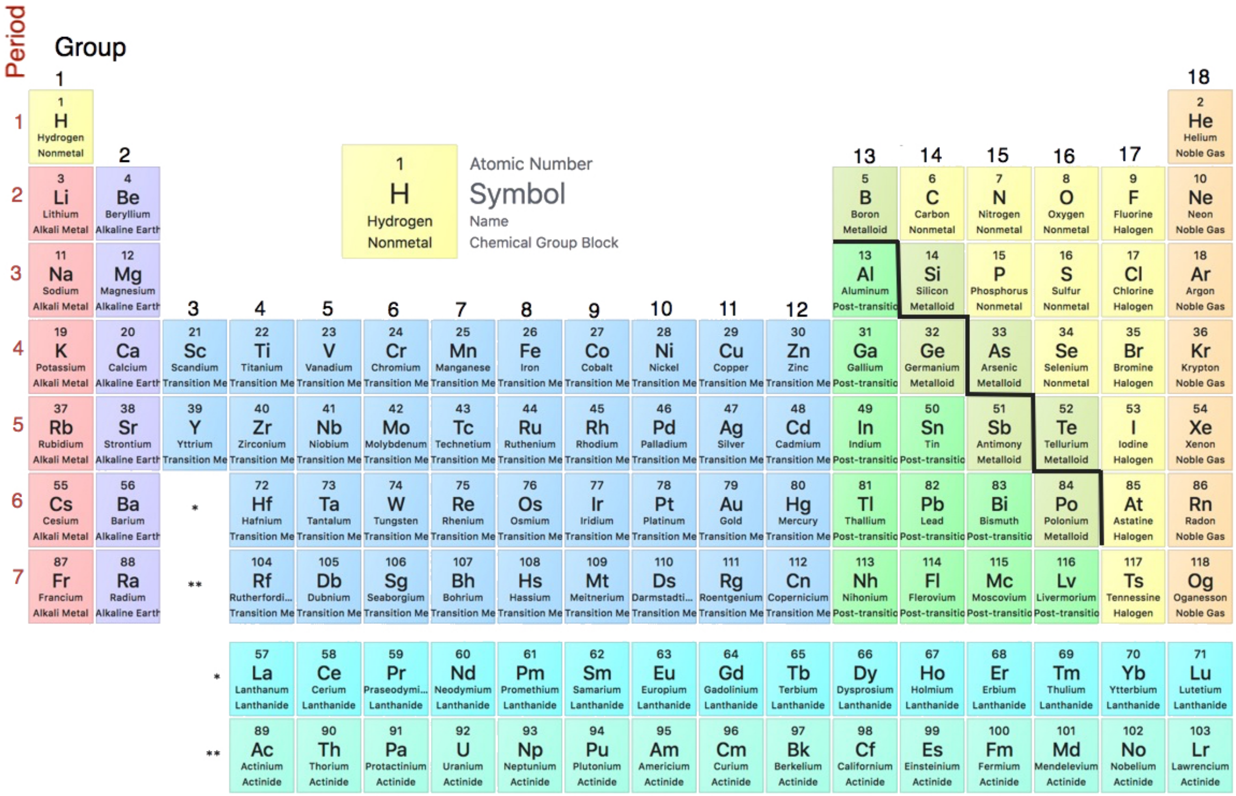
4: Structure of the Atom

4.1: 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.

The **periodic table** organizes all the known elements in order of atomic number as well as on the basis of their chemical properties. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element’s symbol.



Group

1
H
Hydrogen
Nonmetal — Atomic Number
Symbol
Name
Chemical Group Block

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
2	3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
3	11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth											13 Al Aluminum Post-transitio	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
4	19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth	21 Sc Scandium Transition Me	22 Ti Titanium Transition Me	23 V Vanadium Transition Me	24 Cr Chromium Transition Me	25 Mn Manganese Transition Me	26 Fe Iron Transition Me	27 Co Cobalt Transition Me	28 Ni Nickel Transition Me	29 Cu Copper Transition Me	30 Zn Zinc Transition Me	31 Ga Gallium Post-transitio	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
5	37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth	39 Y Yttrium Transition Me	40 Zr Zirconium Transition Me	41 Nb Niobium Transition Me	42 Mo Molybdenum Transition Me	43 Tc Technetium Transition Me	44 Ru Ruthenium Transition Me	45 Rh Rhodium Transition Me	46 Pd Palladium Transition Me	47 Ag Silver Transition Me	48 Cd Cadmium Transition Me	49 In Indium Post-transitio	50 Sn Tin Post-transitio	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
6	55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth	*	72 Hf Hafnium Transition Me	73 Ta Tantalum Transition Me	74 W Tungsten Transition Me	75 Re Rhenium Transition Me	76 Os Osmium Transition Me	77 Ir Iridium Transition Me	78 Pt Platinum Transition Me	79 Au Gold Transition Me	80 Hg Mercury Transition Me	81 Tl Thallium Post-transitio	82 Pb Lead Post-transitio	83 Bi Bismuth Post-transitio	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
7	87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth	**	104 Rf Rutherfordi... Transition Me	105 Db Dubnium Transition Me	106 Sg Seaborgium Transition Me	107 Bh Bohrium Transition Me	108 Hs Hassium Transition Me	109 Mt Meitnerium Transition Me	110 Ds Darmstadti... Transition Me	111 Rg Roentgenium Transition Me	112 Cn Copernicium Transition Me	113 Nh Nihonium Post-transitio	114 Fl Flerovium Post-transitio	115 Mc Moscovium Post-transitio	116 Lv Livermorium Post-transitio	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
			*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymi... Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
			**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide

Figure 4.1.1: 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**. 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 4.1.2. 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 4.1.2, **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.

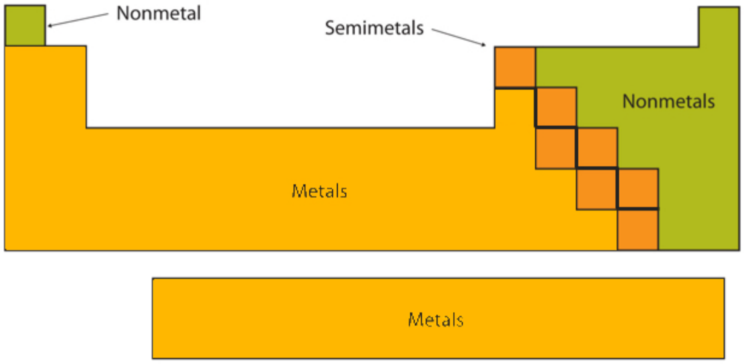


Figure 4.1.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

✓ Example 4.1.1

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 4.1.2, 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 4.1.1

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 4.1.3. 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.

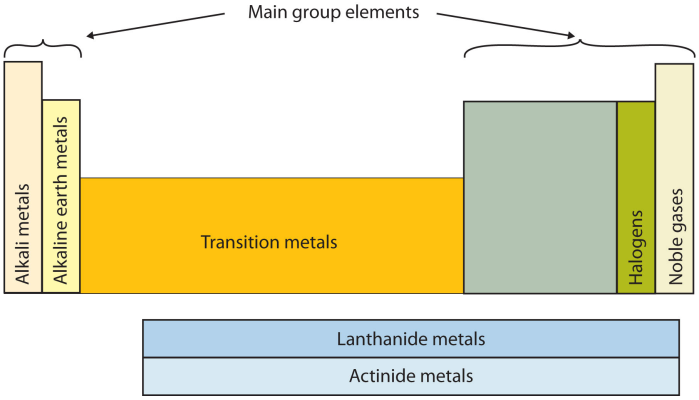


Figure $4.1.3$: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

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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4.2: Some Characteristics of Different Groups

Learning Objectives

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

The periodic table is useful for understanding atomic properties that show **periodic trends**. Periodic trends are specific patterns that occur with an increase in atomic number (number of protons). These trends exist because of the changing structure of atoms as the numbers of protons and electrons increase.

One important atomic property is the **atomic radius**, which is a measure of the atomic size, usually the distance from the nucleus to the outer electron shell. A clear periodic trend can be observed when atomic radius is plotted vs. atomic number (Figure 4.2.1). The radii generally decrease along each row of the table and increase down each group. The radius increases sharply between the noble gas at the end of each period and the alkali metal at the beginning of the next period. The largest atoms are found in the lower left corner of the periodic table and the smallest (with the exception of hydrogen) are found in the upper right corner.

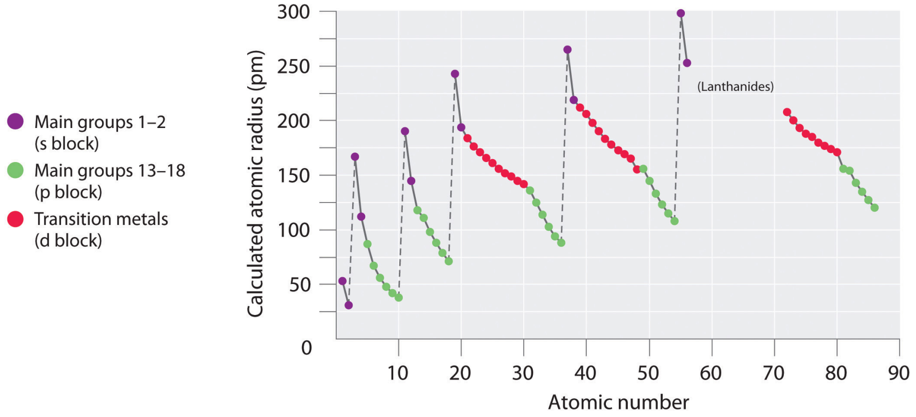


Figure 4.2.1: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

The melting point is a metric of the energy required to transform the solid phase of a substance into a liquid. Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond. The melting points exhibit comparable, albeit more complex, periodic trends as observed in the atomic radii (Figure 4.2.2). Key feature of these trends are:

- Metals generally possess a *high melting point*.
- Most non-metals possess *low melting points*.
- The non-metal carbon possesses *the highest melting point of all the elements*. The semi-metal boron also possesses a high melting point.

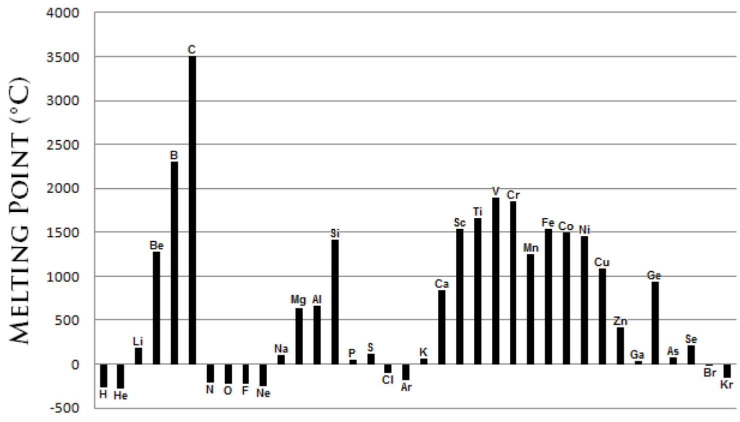


Figure 4.2.2: A plot of melting point vs. atomic number show a periodic trend.

The trends of the atomic radii and melting points (and other chemical and physical properties of the elements) can be explained by the electron shell theory of the atom discussed in the following sections.

Element Characteristics By Group

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 –** lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) are soft, shiny, and highly reactive metals. 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. *Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal.*
- **Group 2: The Alkaline Earth Metals –** beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) are shiny, slivery-white, somewhat reactive metals. 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 –** fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At) are nonmetals. 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).
- **Group 18: The Noble Gases –** helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are gases at room temperature and pressure. Because the noble gases are composed of only single atoms, they are called monatomic. 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.

✓ Example 4.2.1: Groups

Provide the family/group names and period numbers (horizontal values) of each element.

a. Li
b. Ar
c. Ra

Solution:

a. Lithium is an alkali metal. It is located in period two.
b. Argon is a noble gas. It is located in period three.
c. Radium is an alkaline metal. It is located in period seven.

✓ Example 4.2.2: Classification of Elements

Provide elemental names for the following combinations:

a. The alkali metal in period three.
b. The halogen in period two
c. A metalloid in period four
d. A transition metal in period three

Solution:

a. Sodium
b. Fluorine
c. Germanium or Arsenic
d. There are no transition metals in period three (gotcha!)

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.

4.3: Electronic Structure of Atoms

Learning Objectives

- Describe how electrons are grouped within atoms into shells, subshells, and orbitals.

You now know that the periodic table is arranged in groups and periods (columns and rows) based on chemical and physical properties of the different elements. The first element, hydrogen has one proton and one electron and as you move right across the rows, each subsequent element has one additional proton and electron. You may have asked yourself, why are periodic trends observed across the rows and down the groups? Or, why do the rows have different numbers of elements, giving the table a unique shape?

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

In the early 1900's, scientists learned that an electron in an atom can have *only* certain fixed values of energy. We call this idea **quantized** energy. Much like the steps on a staircase do not have half or quarter levels in between, or the keys on a piano don't have notes in between, there are no energy levels in between each allowable energy value. Figure $4.3.1$ shows a simple model of an atom showing different rings around the nucleus of the atom that correspond to the idea of energy levels.

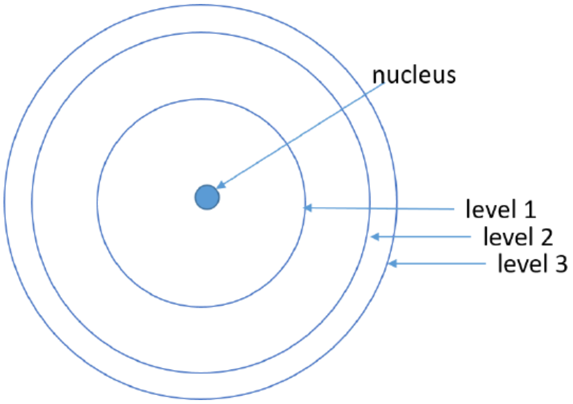


Figure $4.3.1$: A simple model to depict the idea of energy levels within an atom. Each ring represents a region of space that the electron in that energy level is confined within.

Figure $4.3.1$ does not give a full picture of where the electrons are located within an atom. For a better understanding we need quantum mechanics.

Quantum mechanics uses a mathematical treatment of the atom that explains the behavior of electrons as if they were acting as a wave, not as particles. It shows that within each level (shell), electrons are further arranged in sublevels and these sublevels are broken into specific regions of space that we call orbitals. So the exact location of the electron is in a specific orbital, that's in a specific subshell, that's in a specific shell. Additionally two electrons can occupy one orbital and when they do they align with opposite "spin" (more on that soon).

Four **quantum numbers** specify the location of each electron in the atom. Much like your home address can be used to locate you in a specific state, city, street, and house number, the first three quantum numbers identify approximately where electrons are in an atom. The fourth quantum number describes the orientation of an individual electron's electromagnetic field, its **spin**. The theory and mathematics behind these four quantum numbers are well beyond the scope of this textbook, however, it is useful to learn some of the basics in order to understand how atoms behave and interact with (react) with other atoms.

Electron Arrangements: Shells, Subshells, and Orbitals

Electrons are organized according to their energies into sets called **shells** identified by the integers 1, 2, 3, 4, 5, 6, & 7 (mathematically the value can be any integer but in practice we typically only use values up to 7). A simplified view of these shells is presented in Figure $4.3.1$ where each ring/level represents a shell. The lowest energy shell is shell 1 (level 1) and the energy values increase from there. Electrons in a higher-energy shell will spend more time farther from the nucleus than electrons in a lower-energy shell.

Shells are further divided into **subshells**, labeled *s*, *p*, *d*, or *f*. The first shell has only one subshell, *s*. The second shell has two subshells, *s* and *p;* the third shell has three subshells, *s*, *p*, and *d*, and the fourth shell has four subshells, *s*, *p*, *d*, and *f*. Within each subshell, electrons are arranged into different numbers of **orbitals**, an *s* subshell is made up of one *s* orbital, a *p* subshell has three *p* orbitals, a *d* subshell, five *d* orbitals, and an *f* subshell, seven *f* orbitals. Each orbital has a different shape and orientation around the nucleus (Figure 4.3.2), however, rather than representing an orbit, as the name suggests, orbitals define a boundary for the region of space where a given electron is most likely to be found. And again, a single orbital can hold up to two electrons each with a different spin.

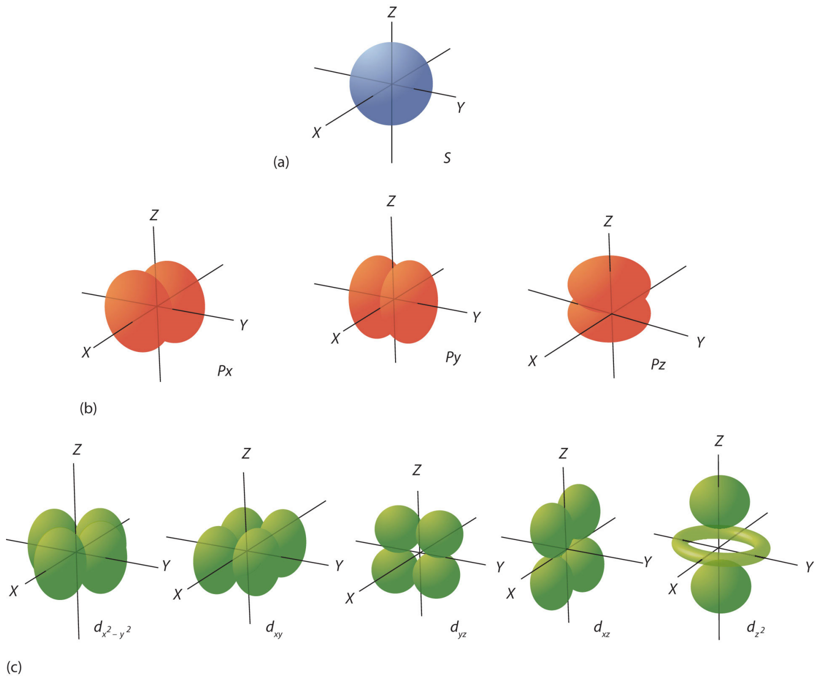


Figure 4.3.2: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the d_{z^2} orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

You can visualize or imagine that the second shell would have the all four orbitals shown in parts (a) and (b) of Figure 4.3.2 all centered around the nucleus and enclosed within the second ring of Figure 4.3.1. The third shell would include *another set* of all the same types (an s and three p) as well as the additional orbitals in row (c) of Figure 4.3.2.

It is important to note that according to quantum theory, there are specific *allowed* combinations of quantum numbers and others that are not allowed. For example, shell two can only have two subshells, *s* with one orbital and *p* with 3 orbitals, therefore, this shell can hold a maximum of eight electrons (four orbitals times two electrons each). It takes practice to learn the allowed combinations as shown in Table 4.3.1 but it is helpful to visualize the atom as a sphere with the nucleus in the center. Close to the nucleus, there is a smaller amount of space for electrons – a smaller shell. As the number of electrons increases, the shells that hold the electrons get larger and thus further away from the nucleus.

Table 4.3.1: Shells and Subshells

Shell (*n*)	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
1	1	*1s*	1	2	2
2	2	*2s* and *2p*	1, 3	2, 6	8

Shell (*n*)	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
3	3	*3s*, *3p*, and *3d*	1, 3, 5	2, 6, 10	18
4	4	*4s*, *4p*, *4d*, and *4f*	1, 3, 5, 7	2, 6, 10, 14	32

All of this information about the shell, subshell, and orbital is put together to make up the "address" for an electron and all of the addresses for all the electrons in an atom make up the **electron configuration**, which is described more later.

4.4: Electron Configurations

Learning Objectives

- Describe how electrons are arranged in an atom using electron configurations.

Previously we discussed the concept of electron *shells*, *subshells*, *orbitals*, and electron *spin*. 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. 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 $\mathbf{1s^1}$ (spoken as "one-ess-one") to describe the electron arrangement or distribution of electrons in hydrogen. This structure is called an **electron configuration** and is unique to hydrogen.

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

The 1*s* subshell can hold a maximum of 2 electrons, so the electron configuration for a lithium atom, which has three electrons, 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 and the lower energy orbital, which is the 2*s* orbital. Therefore, we write the electron configuration of a lithium atom as $\mathbf{1s^2 2s^1}$ (spoken as "one-ess-two two-ess-one").

The shell diagram for a lithium atom (Figure 4.4.1). 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.

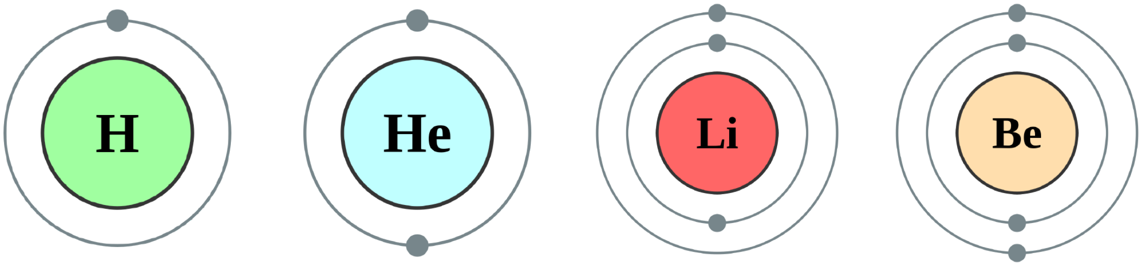


Figure 4.4.1: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

There are a set of general rules that are used to figure out the electron configuration of an atomic species: **Aufbau Principle**, **Hund's Rule** and the **Pauli-Exclusion Principle**.

- **Rule 1 (Aufbau Principle):** Electrons occupy the lowest-energy orbitals (closest to the nucleus) possible, starting with 1*s*, then 2*s*, 2*p*, and continuing on to higher energy (further away from the nucleus). Shells increase in energy in order from 1 to 2 to 3, and so on. Within these shells, an *s* subshell is the lowest energy followed by *p*, then *d*, then *f*.
- **Rule 2 (Hund's Rule):** When electrons occupy degenerate orbitals (i.e. same shell and subshell), they must first singly occupy (half-fill) each empty orbital in a subshell before double occupying (completely filling) them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all spin up or all spin down). For example, all three *p* orbitals in a *p* subshell will have one electron before a single *p* orbital contains two electrons.
- **Rule 3 (Pauli-Exclusion Principle):** Each electron is described with a unique set of four quantum numbers (a unique address). Therefore, if two electrons occupy the same orbital, they must have different spins. This is the reason all orbitals can hold a maximum of two electrons.

Continuing on the periodic table to the next largest atom, beryllium, with 4 electrons, the electron configuration is $1s^2 2s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms, starting with boron, begin filling the 2*p* subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

- B: $1s^2 2s^2 2p^1$

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

At the end of the period the element neon, has filled the 2*s*, and 2*p* subshells, which completes the second shell. Now atoms with more electrons now must begin the third shell starting with the 3*s* subshell. 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.

Table 4.4.1: Electron Configurations of the First 20 Elements

Atomic Number	Element Symbol	Outermost Shell	Electron Configuration	Noble Gas Configuration
1	H	1	$1s^1$	$1s^1$
2	He	1	$1s^2$	$1s^2$
3	Li	2	$1s^22s^1$	[He] $2s^1$
4	Be	2	$1s^22s^2$	[He] $2s^2$
5	B	2	$1s^22s^22p^1$	[He] $2s^22p^1$
6	C	2	$1s^22s^22p^2$	[He] $2s^22p^2$
7	N	2	$1s^22s^22p^3$	[He] $2s^22p^3$
8	O	2	$1s^22s^22p^4$	[He] $2s^22p^4$
9	F	2	$1s^22s^22p^5$	[He] $2s^22p^5$
10	Ne	2	$1s^22s^22p^6$	[He] $2s^22p^6$
11	Na	3	$1s^22s^22p^63s^1$	[Ne] $3s^1$
12	Mg	3	$1s^22s^22p^63s^2$	[Ne] $3s^2$
13	Al	3	$1s^22s^22p^63s^23p^1$	[Ne] $3s^23p^1$
14	Si	3	$1s^22s^22p^63s^23p^2$	[Ne]$3s^23p^2$
15	P	3	$1s^22s^22p^63s^23p^3$	[Ne] $3s^23p^3$
16	S	3	$1s^22s^22p^63s^23p^4$	[Ne] $3s^23p^4$
17	Cl	3	$1s^22s^22p^63s^23p^5$	[Ne] $3s^23p^5$
18	Ar	3	$1s^22s^22p^63s^23p^6$	[Ne] $3s^23p^6$
19	K	4	$1s^22s^22p^63s^23p^64s^1$	[Ar] $4s^1$
20	Ca	4	$1s^22s^22p^63s^23p^64s^2$	[Ar] $4s^2$

Noble Gas Configuration

The electron configuration of sodium is $1s^22s^22p^63s^1$ (Table 4.4.1). The first ten electrons of the sodium atom are the inner-shell electrons and the configuration of just those ten electrons is exactly the same as the configuration of the element neon $(Z = 10)$. This provides the basis for a shorthand notation for electron configurations called the **noble gas configuration**, which atom consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons. So for sodium, we make the substitution of $[\text{Ne}]$ for the $1s^22s^22p^6$ part of the configuration. Sodium's noble gas configuration becomes $[\text{Ne}]\,3s^1$.

The electron filling diagram shown below in Figure 4.4.2 is useful in remembering the order for electrons to occupy shells and subshells. Although it is much easier to use the periodic table as a guide for electron filling as you will see in the next section.

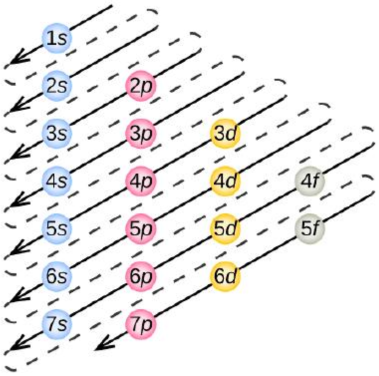


Figure 4.4.2: The order of electron filling in an atom. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

✓ Example 4.4.1: Electronic Configuration of Phosphorus Atoms

Using Figure 4.4.2 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 4.4.1: Electronic Configuration of Chlorine Atoms

Using Figure 4.4.2 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 $1s^2 2s^2 2p^6 3s^2 3p^5$.

Orbital Diagrams

An **orbital diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital diagram, the individual orbitals are shown as squares and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its shell and sublevel. Electrons are indicated by arrows inside of the squares. An arrow pointing upwards indicates one spin direction, while a downward pointing arrow indicates the other direction. The orbital filling diagrams for hydrogen, helium, and lithium are shown in the figure below.

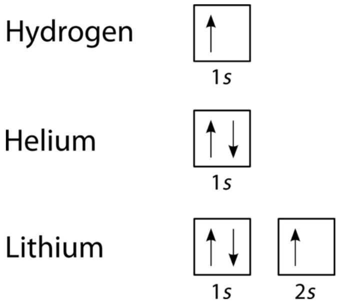


Figure 4.4.3: Orbital diagrams for hydrogen, helium, and lithium.

According to the Aufbau Principle, sublevels and orbitals are filled with electrons in order of increasing energy. Since the s sublevel consists of just one orbital, the second electron simply pairs up with the first electron as in helium. The next element is lithium and necessitates the use of the next available sublevel, the $2s$.

The orbital diagram for carbon is shown in Figure $4.4.10$. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital (Hund's Rule).

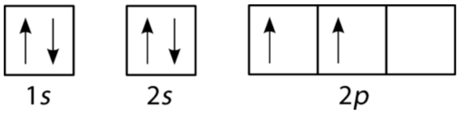


Figure $4.4.4$: Orbital diagram for carbon.

Oxygen has four $2p$ electrons. After each $2p$ orbital has one electron in it, the fourth electron can be placed in the first $2p$ orbital with a spin opposite that of the other electron in that orbital.

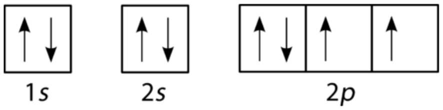


Figure $4.4.5$: Orbital diagram for oxygen.

If you keep your papers in manila folders, you can pick up a folder and see how much it weighs. If you want to know how many different papers (articles, bank records, or whatever else you keep in a folder), you have to take everything out and count. A computer directory, on the other hand, tells you exactly how much you have in each file. We can get the same information on atoms. If we use an orbital filling diagram, we have to count arrows. When we look at electron configuration data, we simply add up the numbers.

✓ Example $4.4.3$: Carbon Atoms

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

Solution

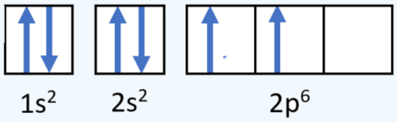
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

Use the order of fill diagram to draw an orbital filling diagram with a total of six electrons. Follow Hund's rule. Write the electron configuration.

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

Electron configuration $1s^22s^22p^2$

Step 3: Think about your result.

Following the 2s sublevel is the 2p, and p sublevels always consist of three orbitals. All three orbitals need to be drawn even if one or more is unoccupied. According to Hund's rule, the sixth electron enters the second of those p orbitals and has the same spin as the fifth electron.

- **9.6: Quantum-Mechanical Orbitals and Electron Configurations** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

4.5: Electron Configurations and the Periodic Table

Learning Objectives

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

Remember, that the periodic table as a tool for organizing the known chemical elements(Figure 4.5.1). The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns. Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: the shape of the periodic table mimics the filling of the subshells with electrons.

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

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the n = 1 shell is filled. These two elements make up the first row of the periodic table (Figure 4.5.1)

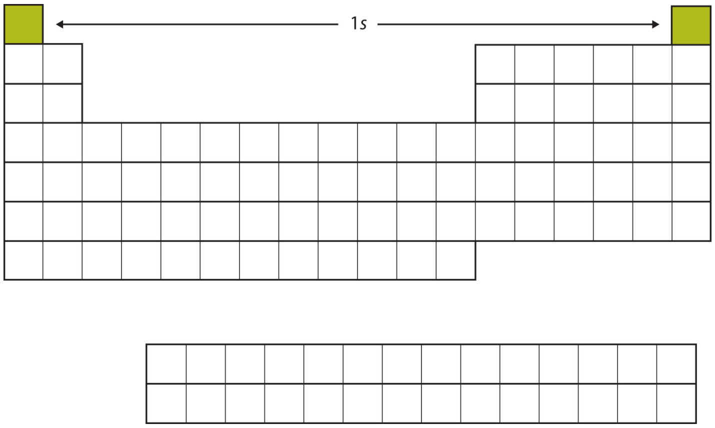


Figure 4.5.1: The 1s Subshell. H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2s subshell. Figure 4.5.2 shows that these two elements are adjacent on the periodic table.

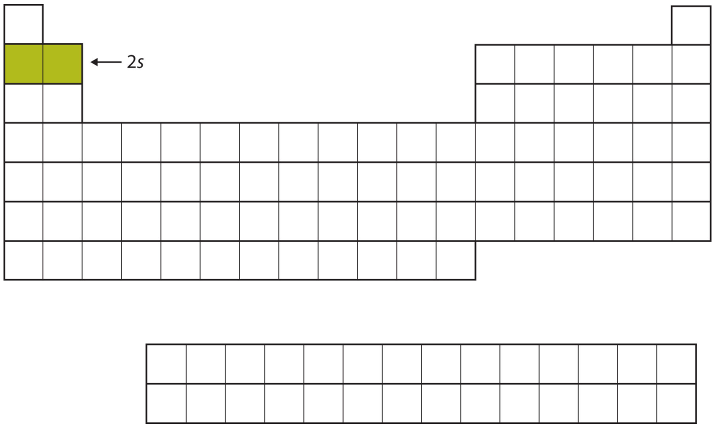


Figure 4.5.2: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2p subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 4.5.3).

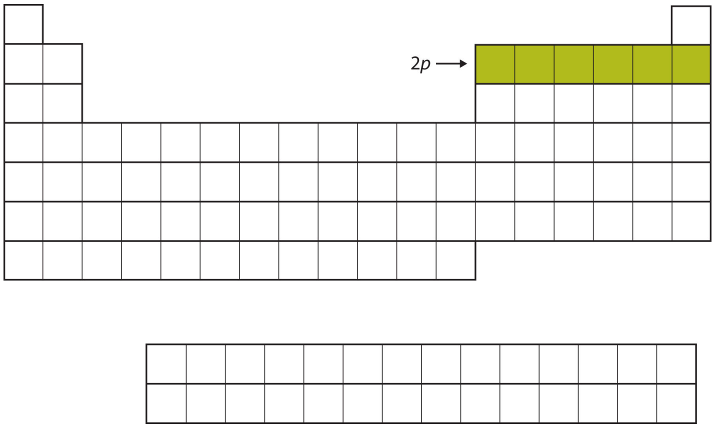


Figure 4.5.3: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 4.5.4).

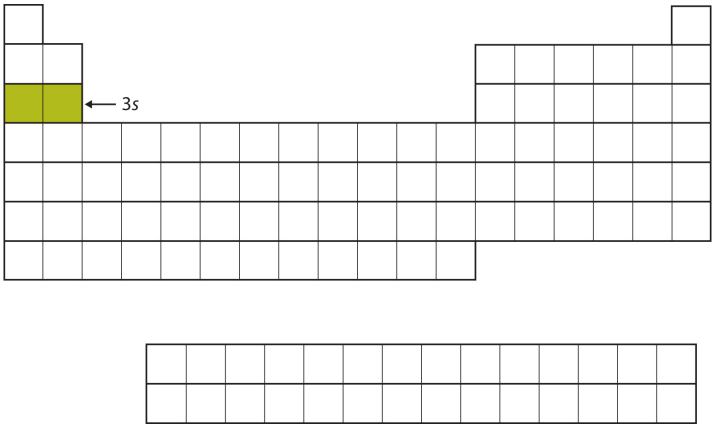


Figure 4.5.4: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 4.5.5).

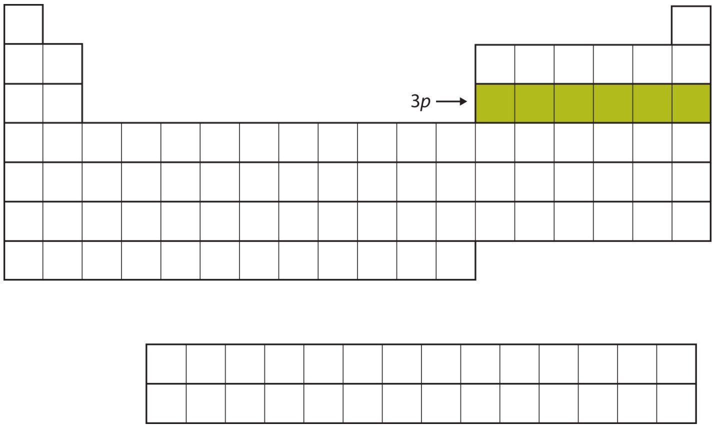


Figure 4.5.5: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 4.5.6).

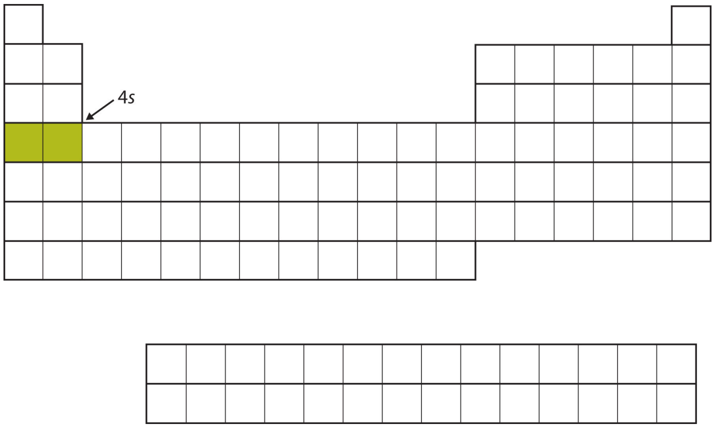


Figure 4.5.6: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 4.5.7).

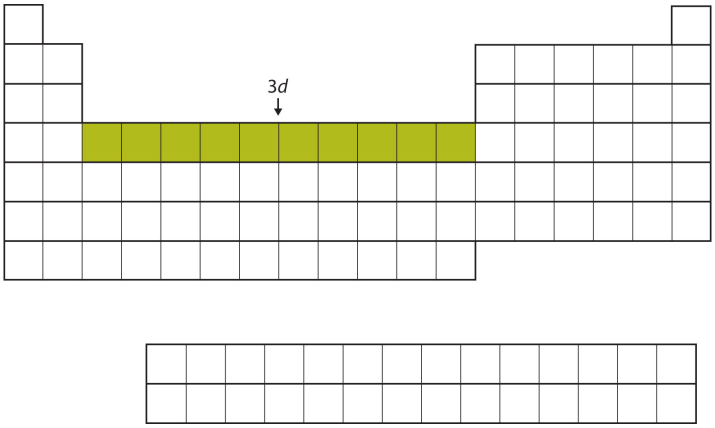


Figure 4.5.7: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 4.5.8 shows the blocks of the periodic table.

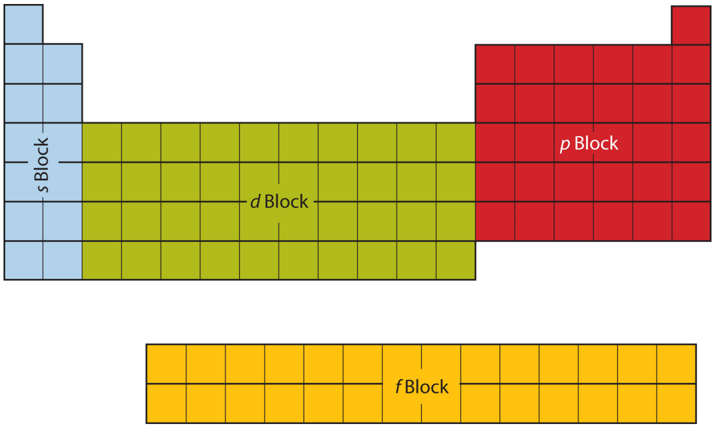


Figure 4.5.8: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Table shows first column of the periodic table and their electron configurations.

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

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

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

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure $4.5.9$. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

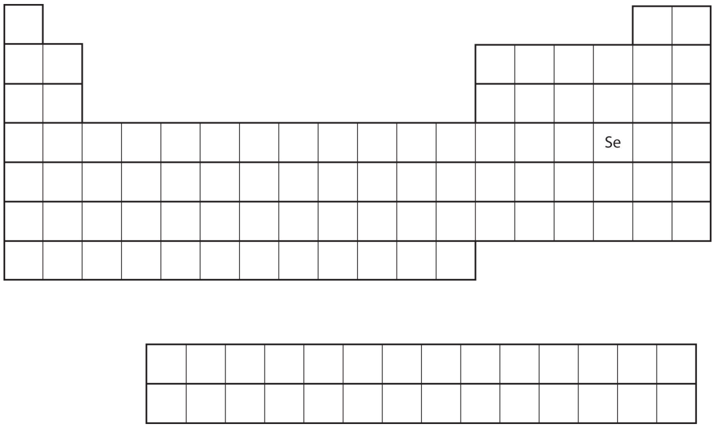


Figure $4.5.9$: Selenium on the Periodic Table

✓ Example $4.5.1$

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure $4.5.10$).

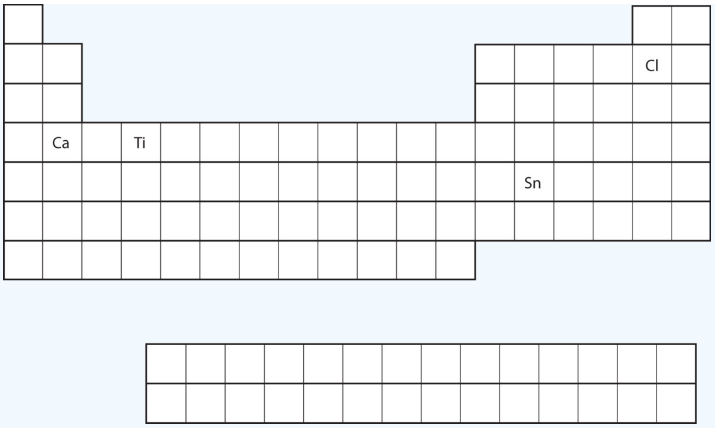


Figure 4.5.10: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

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

Exercise 4.5.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 4.5.10

a. Ti
b. Cl

Answer a

$[Ar]4s^2 3d^2$

Answer b

$[Ne]3s^2 3p^5$

Example 4.5.2: Aluminum

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 4.5.2. Place two electrons in the 1s subshell ($\mathbf{1s^2}$).

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

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

The electron configuration of Aluminum is $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^1}$

Exercise 4.5.2

Using Figure 4.5.2 as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure 4.5.2 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**

Summary

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

4.6: Electron-Dot Symbols

Learning Objective

- Draw a Lewis electron dot symbol for a given atom.

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

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

$$\mathbf{H}\cdot \tag{4.6.1}$$

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

$$\dot{\mathbf{H}} \; or \; \cdot\mathbf{H} \; or \; \underset{\cdot}{\mathbf{H}} \tag{4.6.2}$$

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

$$\mathbf{He}\!: \tag{4.6.3}$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1*s* subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^22s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathbf{Li}\cdot \tag{4.6.4}$$

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

$$\mathbf{Be}\!: \tag{4.6.5}$$

The next atom is boron. Its valence electron shell is $2s^22p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

$$\dot{\mathbf{B}}\mathbf{e}\!: \tag{4.6.6}$$

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

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

$$\cdot\dot{\mathbf{C}}\!: \tag{4.6.7}$$

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

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\!: \tag{4.6.8}$$

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

$$\cdot\underset{\cdot}{\ddot{\mathbf{O}}}\!: \tag{4.6.9}$$

Fluorine and neon have seven and eight dots, respectively:

$$:\underset{\cdot}{\ddot{\mathbf{F}}}\!: \tag{4.6.10}$$

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{Ne}}}: \tag{4.6.11}$$

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

Example 4.6.1:

What is the electron-dot symbol for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the $3s$ electrons:

$$\dot{Al}:$$

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

$$\cdot\overset{\cdot}{\underset{\cdot\cdot}{\mathbf{Se}}}:$$

Exercise 4.6.1

What is the electron-dot symbol for each element?

a. phosphorus
b. argon

Answer

$$\cdot\overset{\cdot}{\underset{\cdot}{\mathbf{P}}}:$$

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{Ar}}}:$$

Summary

- Lewis electron-dot symbols use dots to represent valence electrons around an atomic symbol.

4.7: Electron Arrangments (Worksheet)

Name: ________________________________

Section: _______________________________

Student ID#:____________________________

Work in groups on these problems. You should try to answer the questions without referring to your textbook. If you get stuck, try asking another group for help.

Q1.

Write the full ground-state electron configuration and orbital diagram for the following:

a. Rb

b. Ge

c. Ar

d. Br

e. Mg

f. Se

g. Cl

h. Si

i. Sr

Q2.

Write the condensed electron configuration for the following, and indicate valence and core electrons:

a. Ti

b. Cl

c. Hg

d. Ba

Q3.

Write the electron configuration for the following ions:

a. Be^{2+}

b. Sc^{+1}

c. As^{2-}

d. N^{3-}

CHAPTER OVERVIEW

5: Compounds and Bonding

SECTION OVERVIEW

5.1: Ionic Compounds

When you think of bonding, you may not think of ions or molecules. Like most of us, you probably think of bonding between people. Like people, molecules bond — and some bonds are stronger than others. It's hard to break up a mother and baby, or a molecule made up of one oxygen and two hydrogen atoms! 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.

5.1.1: Ions

Learning Objectives

- Describe how an ion is formed.
- Distinguish the difference between the two types of ions.

Ions

As introduced previously, atoms contain a nucleus with neutrons and positively charged protons, surrounded by negatively charged electrons. In an atom, the total number of electrons, negative charge, *equals* the total number of protons, positive charge, and therefore, atoms are electrically neutral or uncharged. If an atom loses or gains electrons, it will become a positively or negatively charged particle, called an **ion**. The *loss* of one or more electrons results in more protons than electrons and an overall positively charged ion, called a **cation**. For example, a sodium atom with one less electron is a cation, Na^+, with a +1 charge (Figure 5.1.1.1).

Figure 5.1.1.1: A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. When it loses an electron, the resulting sodium cation has one more proton (11) than electrons (10), giving it an overall positive one charge, Na+.

When an atom *gains* one or more electrons, it becomes a negatively charged **anion**, because there are more electrons than protons. When chlorine gains one electron it forms a chloride ion, Cl^-, with a –1 charge (Figures 5.1.1.2)

> The names for positive and negative ions are pronounced CAT-eye-ons (cations) and ANN-eye-ons (anions), respectively.

Figure 5.1.1.2: A chlorine atom (Cl) has equal numbers of protons and electrons (17) and is uncharged. When it gains an electron, the resulting chlorine anion has one more electron (18) than protons (17), giving it an overall negative one charge, Cl–.

Note Naming Ions

Cations are named using the element name plus "*ion*" to indicate it is charged. Anions are named by changing the element name ending to "*ide*". For example, a magnesium ion is formed when neutral magnesium loses electrons and a fluor*ide* ion is formed when neutral fluorine gains electrons.

Example 5.1.1.1

A calcium (Ca) atom loses two electrons and a sulfur (S) atom gains two electrons. Determine if the resulting ions are cations or anions? Write the ion symbols for each.

Solution

When calcium (Z = 20) gains two electrons the resulting ion will have 18 electrons and 20 protons and therefore a charge of +2 (there are two more positive protons than negative electrons), it is a cation. The symbol for a calcium ion is Ca^{2+}.

When sulfur (Z = 16) gains two electrons the resulting ion will have 18 electrons and 16 protons and therefore a charge of –2 (there are two more negative electrons than positive protons), it is an anion. The symbol for a sulf*ide* ion is S^{2-}.

Key Takeaways

- Ions are formed when atoms gain or lose electrons.
- Ions can be positively charged (cations) or negatively charged (anions).

Contributors

- Lisa Sharpe Elles, University of Kansas

5.1.2: Ions and the Octet Rule

Learning Objectives

- Use the octet rule and electron configurations to determine if an atom will gain or lose electrons forming anions or cations.

Ions are formed when an atom, usually on the left side of the periodic table, *reacts with* and *transfers* one or more electrons to another atom, usually on the right side of the periodic table. These electrons are usually *lost from* or *gained into* the **valence shell**, or outermost energy level (shell). Why do some atoms lose electrons and others gain electrons? How can we predict the number of electrons lost or gained? Which ions are stable and which ions do not form at all? These questions are best answered by looking at electron configurations and considering what is called the **octet rule**, which states that atoms gain or lose electrons to form a stable, noble gas configuration, i.e., a filled subshell containing *eight* electrons. Therefore, it is useful to take a closer look at electron configurations to further illustrate ion formation and electron transfer between atoms.

The electron configuration for sodium shows that there are ten core electrons and one valence electron in the third energy level. When sodium loses the single valence electron, forming the cation Na^+, the electron configuration is now identical to that of neon, a stable noble gas with eight valence electrons.

$$\begin{array}{lcl} \mathrm{Na} & \rightarrow & \mathrm{Na}^+ + \mathrm{e}^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^1 & & 1s^2\ 2s^2\ 2p^6 \end{array} \tag{5.1.2.1}$$

Chlorine also has ten core electrons and valence electrons in the third energy level. However, chlorine has seven valence electrons, one less than the noble gas argon, which has eight valence electrons. Thus, chlorine will gain one electron, forming the anion, $Cl^–$, and achieving a stable noble gas configuration.

$$\begin{array}{lcl} \mathrm{Cl} + \mathrm{e}^- & \rightarrow & \mathrm{Cl}^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5 & & 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 \end{array} \tag{5.1.2.2}$$

The octet rule and the periodic table can be used to predict what ions will form; main group elements on the left side of the periodic table (metals in groups 1, 2, and 13) tend to lose electrons (form cations) to achieve the same electron configuration as the noble gas just *before* them in the table. The number of electrons the atom will lose depends on what group the atom is in, i.e., how many valence electrons it has. Main group elements on the right side of the periodic table (nonmetals in groups 15-17) will gain electrons to achieve the same electron configuration as the noble gas just *after* them in the table. Again, the number of electrons the atom will gain depends on the number of valence electrons it has and how many are needed to reach the filled subshell, eight electrons.

Note Violation of the Octet Rule

It is *not impossible* to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even *more* energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the $n = 2$ shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Example 5.1.2.1

Write the electron configuration of aluminum atom ($Z = 13$) and underline the *valence electrons*. How many electrons are gained/lost to form an aluminum ion? Write the symbol and the electron configuration for an aluminum ion.

Solution

The electron configuration of Al atom is $1s^22s^22p^63s^23p^1$. Aluminum has three valence electrons in the third energy level, ($3s^23p^1$). The cation, Al^{3+}, is formed when these three valence electrons are **lost**, leaving the configuration for the noble gas neon, $1s^22s^22p^6$.

? Exercise 5.1.2.1

Write the electron configuration of oxygen atom (Z = 8) and underline the valence electrons. How many electrons are gained/lost to form an oxide ion? Write the symbol and electron configuration for oxide ion.

Answer

> The electron configuration of O atom is $1s^22s^22p^4$. Oxygen has six valence electrons in the second energy level, ($2s^22p^4$). The anion O^{2-} is formed when two electrons are **gained** in the valence shell. The resulting electron configuration, $1s^22s^22p^6$, which is also identical to the configuration for the noble gas neon.

5.1.3: Ions of Some Common Elements

Learning Objectives

- Become familiar with the charge of some common ions.
- Use the periodic table to predict ion charge.

In many cases, elements that belong to the *same group* (vertical column) on the periodic table form ions with the *same charge* because they have the *same number* of valence electrons. Thus, as introduced previously, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a +1 charge. Ions made from alkaline earth metals, the second group on the periodic table, have a +2 charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a −1 charge. Figure $5.1.3.1$ shows how the charge on many ions can be predicted by the location of an element on the periodic table.

Some elements, especially transition metals, can form ions with variable charges. Figure $5.1.3.1$ shows the characteristic charges for some of these ions. Notice that there is no simple pattern for transition metal ions (or for the larger main group elements) as there is with the main group ions. This is because the transition metals have electrons in *d* subshell and do not follow the octet rule. In order for an element such as iron (Fe) to achieve the same noble gas configuration of argon (Ar), it would need to lose 6 electrons in the *3d* subshell and 2 electrons in the *4s* subshell. An iron ion with a charge of +8 is not very likely, therefore, the octet rule is not applicable to transition elements.

Note

For a multiply-charged ion, the correct convention is to write the charge number first followed by the sign. For example, the barium cation is written Ba^{2+}, not Ba^{+2}.

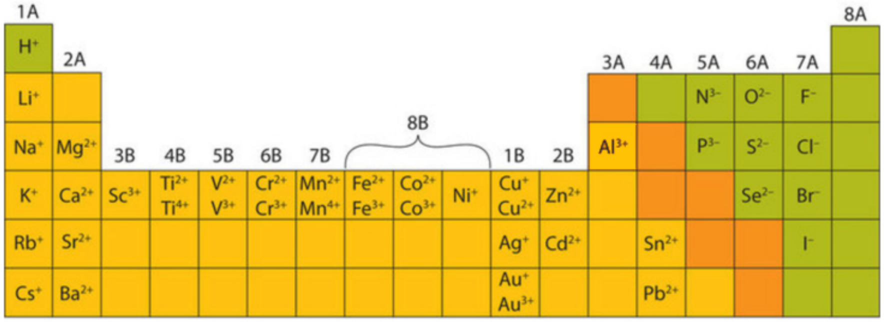


Figure $5.1.3.1$: Common ions formed by specific elements on the periodic table. The charge that a representative (main group element) acquires when it becomes an ion is related to the location on the periodic table. Note that some metal atoms, specifically the transition elements, commonly form ions with variable charges.

ple

Which of these ions is *not likely* to form?

a. Mg^+
b. K^+

Solution

(a) Mg is in Group 2A and has two valence electrons. It achieves octet by losing two electrons to form Mg^{2+} cation. Losing only one electron to form Mg^+ does not make an octet, hence, Mg^+ is not likely to form.

ise

Which of these ions is *not likely* to form?

a. S^{3-}
b. N^{3-}

Answer

(a) S is in Group 6A and has six valence electrons. It achieves octet by gaining two electrons to form S^{2-} anion. Gaining three electrons to form S^{3-}does not make it octet, hence, S^{3-} is not likely to form.

5.1.4: Periodic Properties and Ion Formation

Learning Objectives

- Describe ionization energy and electron affinity and how this relates to ion formation trends.

We have seen that elements often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energy

Because atoms do not spontaneously lose electrons, energy is *required* to remove an electron from an atom to form a cation. Chemists define the ionization energy (IE) of an element as the amount of energy needed to remove an electron from the gaseous atom A in its ground state. IE is therefore the energy required for the reaction:

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \text{energy required=IE} \tag{5.1.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($IE > 0$) for the reaction as written in Equation $5.1.4.1$ Larger values of (IE) mean that the electron is more tightly bound to the atom and thus, harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{5.1.4.2}$$

As you move *across* a row on the periodic table, the ionization energies generally tend to increase. This means that elements on the left side of the periodic table lose electrons more easily (requires less energy to remove an electron) than those on the right side of the periodic table. The trend in ionization energy can be explained by considering the trend in atomic radius (explained in an earlier chapter). As you move from left to right on the periodic table, the atomic size decreases and the electrostatic interactions between the nucleus and valence electrons increases, which increases the energy required to remove electrons, thus the (IE) increases.

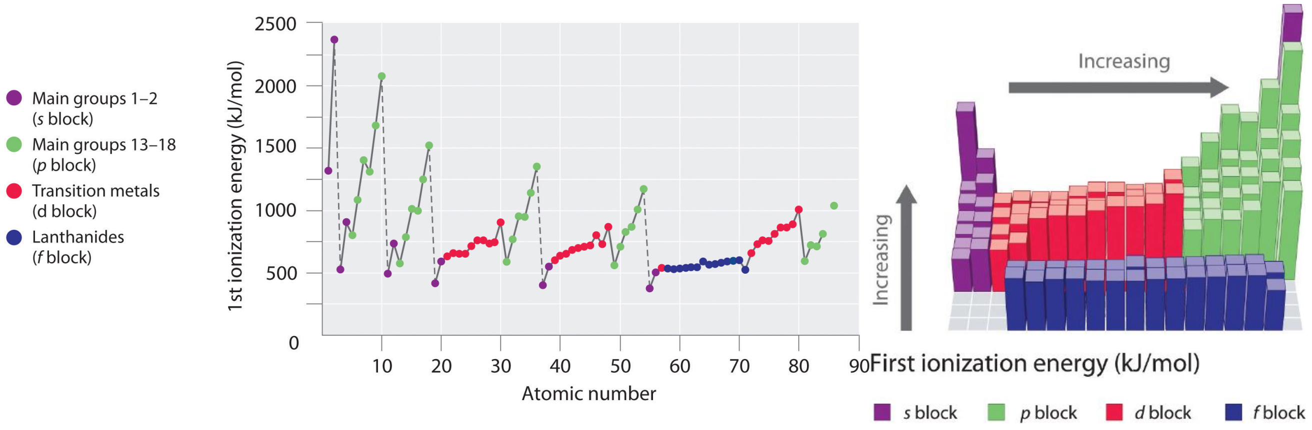


Figure 5.1.4.1: Ionization Energy Trends on the Periodic Table. (Left Figure) A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18). (Right Figure) First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

If you look closely at the trends in ionization energy, you will notice that there are some "exceptions" where you see a decrease in energy rather than an increase. In periods 1 and 2, you can see this decrease in (IE) between groups 2 and 3 and again between groups 5 and 6. These variations in the trend can be further explained by looking closely at the electron configurations of the atoms in question. As you move from magnesium to aluminum, one electron is added to the 3*p* subshell. This 3*p* electron is slightly further from the nucleus (higher in energy) and is therefore, more easy to remove compared to the 3*s* electrons. The decrease between phosphorous and sulfur occurs because the added electron in sulfur is the first to be paired in the *p* subshell. These two electrons in the same *p* orbital repel each other, making the sulfur atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements. This electron is easier to remove because it will lead to more stability.

✓ Example 5.1.4.1: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

? Exercise 5.1.4.1: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer

As

Electron Affinity

The electron affinity (EA) of an element A is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$A(g)+e^{-} \rightarrow A^{-}(g) \qquad \text{energy change}=EA \tag{5.1.4.3}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure 5.1.4.2).

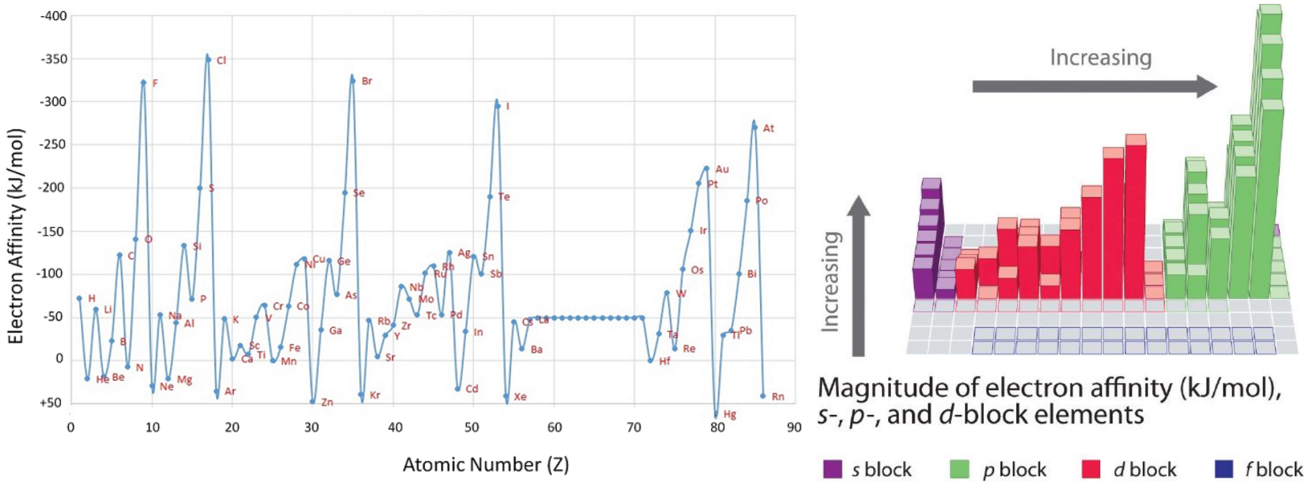


Figure 5.1.4.2: Electron Affinity Trends. (Left) A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies). (Right) Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$\mathrm{Cl(g)} + \mathrm{e}^- \rightarrow \mathrm{Cl}^-\mathrm{(g)} \qquad EA = -346\ kJ/mol \tag{5.1.4.4}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be(g)} + \mathrm{e}^- \rightarrow \mathrm{Be}^-\mathrm{(g)} \qquad EA \geq 0 \tag{5.1.4.5}$$

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as the energy level increases, the extra electrons enter orbitals that are increasingly far from the nucleus, and it is less easy to gain extra electrons forming anions.

✓ Example $5.1.4.2$: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

? Exercise $5.1.4.2$: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer

Rb

5.1.5: Naming Monoatomic Ions

Learning Objectives

- Name monoatomic ions using the defined nomenclature rules.

After learning a few more details about the names of individual ions, you will be a step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

Naming Cations

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, Na^+ is the sodium ion, Al^{3+} is the aluminum ion, Ca^{2+} is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges. Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different ionic compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the ***stock system***, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus, Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na^+ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table 5.1.5.1 lists the elements that use the common system, along with their respective cation names.

Table 5.1.5.1: Names of Some Cations

Element	Charge	Symbol	Common System Name	Stock System Name
chromium	2+	Cr^{2+}	chrom*ous* ion	chromium(II) ion
	3+	Cr^{3+}	chrom*ic* ion	chromium(III) ion
copper	1+	Cu^+	cupr*ous* ion	copper(I) ion
	2+	Cu^{2+}	cupr*ic* ion	copper(II) ion
iron	2+	Fe^{2+}	ferr*ous* ion	iron(II) ion
	3+	Fe^{3+}	ferr*ic* ion	iron(III) ion
lead	2+	Pb^{2+}	plumb*ous* ion	lead(II) ion
	4+	Pb^{3+}	plumb*ic* ion	lead(IV) ion
tin	2+	Sn^{2+}	stann*ous* ion	tin(II) ion
	4+	Sn^{4+}	stann*ic* ion	tin(IV) ion

Naming Anions

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table 5.1.5.2lists the names of some common monatomic ions.

Table 5.1.5.2: Some Monatomic Anions

Element	Charge	Symbol	Name
fluorine	1–	F^-	fluoride ion
chlorine	1–	Cl^-	chloride ion
bromine	1–	Br^-	bromide ion
iodine	1–	I^-	iodide ion
oxygen	2–	O^{2-}	oxide ion
sulfur	2–	S^{2-}	sulfide ion
phosphorous	3–	P^{3-}	phosphide ion
nitrogen	3–	N^{3-}	nitride ion

✓ Example 5.1.5.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. $SO_3{}^{2-}$
d. $NH_4{}^+$
e. Cu^+

Answer a

the calcium ion

Answer b

the sulfide ion (from Table 5.1.5.2)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

the copper(I) ion or the cuprous ion (copper can form cations with either a 1+ or 2+ charge, so we have to specify which charge this ion has

? Exercise 5.1.5.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. $SO_4{}^{2-}$
d. Ba^{2+}
e. $HCO_3{}^-$

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the sulfate ion

Answer d

the barium ion

Answer e

the bicarbonate ion or hydrogen carbonate ion

✓ Example 5.1.5.2

Write the formula for each ion.

a. the bromide ion
b. the phosphate ion
c. the cupric ion
d. the magnesium ion

Answer a

Br^{-}

Answer b

$PO_4{}^{3-}$

Answer c

Cu^{2+}

Answer d

Mg^{2+}

? Exercise 5.1.5.2

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the ferrous ion
d. the potassium ion

Answer a

F^{-}

Answer b

$CO_3{}^{2-}$

Answer c

Fe^{2+}

Answer d

K^{+}

Note Chemistry Is Everywhere: Salt

The element sodium (part [a] in the accompanying figure) is a very reactive metal; given the opportunity, it will react with the sweat on your hands and form sodium hydroxide, which is a very corrosive substance. The element chlorine (part [b] in the accompanying figure) is a pale yellow, corrosive gas that should not be inhaled due to its poisonous nature. Bring these two hazardous substances together, however, and they react to make the ionic compound sodium chloride (part [c] in the accompanying figure), known simply as salt.

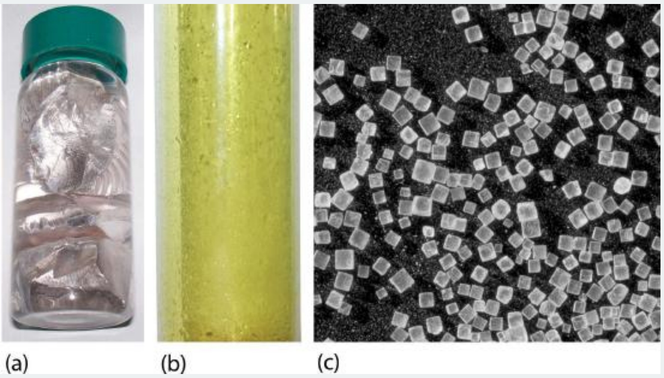


Figure 5.1.5.1: Sodium + Chlorine = Sodium Chloride (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride-salt-which is necessary for our survival. Source: Photo(opens in new window) on the left courtesy of Greenhorn1. Photo(opens in new window) in the center courtesy of Benjah-bmm27, . Photo on the right © Thinkstock.

Salt is necessary for life. Na^+ ions are one of the main ions in the human body and are necessary to regulate the fluid balance in the body. Cl^- ions are necessary for proper nerve function and respiration. Both of these ions are supplied by salt. The taste of salt is one of the fundamental tastes; salt is probably the most ancient flavoring known, and one of the few rocks we eat.

The health effects of too much salt are still under debate, although a 2010 report by the US Department of Agriculture concluded that "excessive sodium intake…raises blood pressure, a well-accepted and extraordinarily common risk factor for stroke, coronary heart disease, and kidney disease."US Department of Agriculture Committee for Nutrition Policy and Promotion, Report of the Dietary Guidelines Advisory Committee on the Dietary Guidelines for Americans, accessed January 5, 2010. It is clear that most people ingest more salt than their bodies need, and most nutritionists recommend curbing salt intake. Curiously, people who suffer from low salt (called *hyponatria*) do so not because they ingest too little salt but because they drink too much water. Endurance athletes and others involved in extended strenuous exercise need to watch their water intake so their body's salt content is not diluted to dangerous levels.

5.1.6: Polyatomic Ions

Learning Objectives

- To identify and name polyatomic ions.

Some ions consist of groups of atoms *covalently* bonded together and have an *overall electric charge*. Because these ions contain more than one atom, they are called **polyatomic ions**. The structures, names, and formulas of some polyatomic ions are found in the below figure and table.

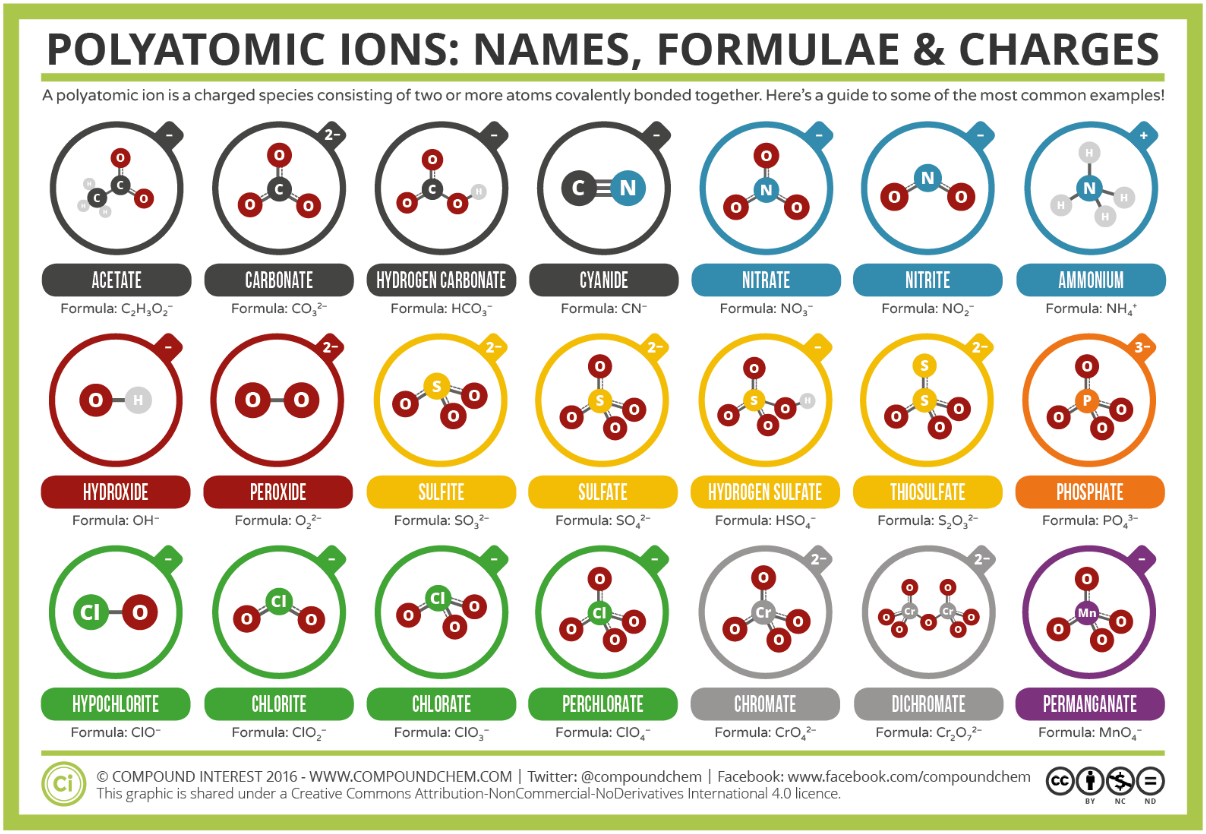


Figure 5.1.6.1: Polyatomic Ions Infographic

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 5.1.6.1 lists the ion names and ion formulas of the most common polyatomic ions. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall −1 charge.

Table 5.1.6.1: Common Polyatomic Ion Names and Formulas

Ion Name	Ion Formula
hyddronium ion	H_3O^+
ammonium ion	NH_4^+
hydroxide ion	OH^-
cyanide ion	CN^-
carbonate ion	CO_3^{2-}
bicarbonate or hydrogen carbonate	HCO_3^-

Ion Name	Ion Formula
acetate ion	$C_2H_3O_2^-$ **or** $CH_3CO_2^-$
nitr**ate** ion	NO_3^-
nitr**ite** ion	NO_2^-
sulf**ate** ion	SO_4^{2-}
sulf**ite** ion	SO_3^{2-}
phosph**ate** ion	PO_4^{3-}
phosph**ite** ion	PO_3^{3-}

Note that only two polyatomic ions in this table are cations, hydronium ion (H_3O^+) and ammonium ion (NH_4^+), the remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "**-ide**" suffix that is typically indicative of negatively-charged ions. The remaining polyatomic anions, which all contain oxygen, in combination with another non-metal, exist as part of a series in which the number of oxygens within the polyatomic unit can vary. A single suffix, "-ide," is insufficient for distinguishing the names of the anions in a related polyatomic series. Therefore, "**-ate**" and "**-ite**" suffixes are employed, in order to denote that the corresponding polyatomic ions are part of a series. Additionally, these suffixes also indicate the relative number of oxygens that are contained within the polyatomic ions. Note that all of the polyatomic ions whose names end in "-ate" contain one more oxygen than those polyatomic anions whose names end in "-ite." Unfortunately, much like the common system for naming transition metals, these suffixes only indicate the *relative* number of oxygens that are contained within the polyatomic ions. For example, both the nitrate ion, symbolized as NO_3^-, and the sulfate ion, symbolized as SO_4^{2-}, share an "-ate" suffix, however, the former contains three oxygens, and the latter contains four. Additionally, both the nitrate ion and the sulfite ion contain three oxygens, but these polyatomic ions do not share a common suffix. Unfortunately, the relative nature of these suffixes mandates that the ion formula/ion name combinations of the polyatomic ions must simply be memorized.

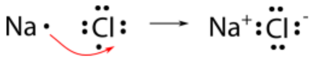
5.1.7: Ionic Bonds

Learning Objectives

- Define an ionic bond, ionic compound, and electrostatic force
- Recognize the complexity of three-dimensional ionic bond interactions involved in ionic compounds

Oppositely charged particles attract each other. This attractive force is often referred to as an **electrostatic attraction**. An **ionic bond** is the electrostatic electrostatic attraction that holds ions together in an **ionic compound**. The strength of the ionic bond is directly dependent upon the quantity of the charges and inversely dependent on the distance between the charged particles. A cation with a 2+ charge will make a stronger ionic bond than a cation with a 1+ charge. A larger ion makes a weaker ionic bond because of the greater distance between its electrons and the nucleus of the oppositely charged ion.

We will use sodium chloride as an example to demonstrate the nature of the ionic bond and how it forms. As you know, sodium is a metal and loses its one valence electron to become a cation. Chlorine is a nonmetal and gains one electron in becoming an anion. However, electrons cannot be simply "lost" to nowhere in particular. A more accurate way to describe what is happening is that a single electron is transferred from the sodium atom to the chlorine atom as shown below.



The ionic bond is the attraction of the Na^+ ion for the Cl^- ion. It is conventional to show show the cation without dots around the symbol to emphasize that the original energy level that contained the valence electron is now empty. The anion is now shown with a complete octet of electrons.

Ionic compounds are held together by attractive electrostatic interactions between cations and anions. In contrast to the simplified electron transfer depicted above for sodium and chlorine, the cations and anions in ionic compounds are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 5.1.7.1). In other words, each ion is attracted to many of its neighboring ions forming a sodium chloride crystal or **ionic solid**.

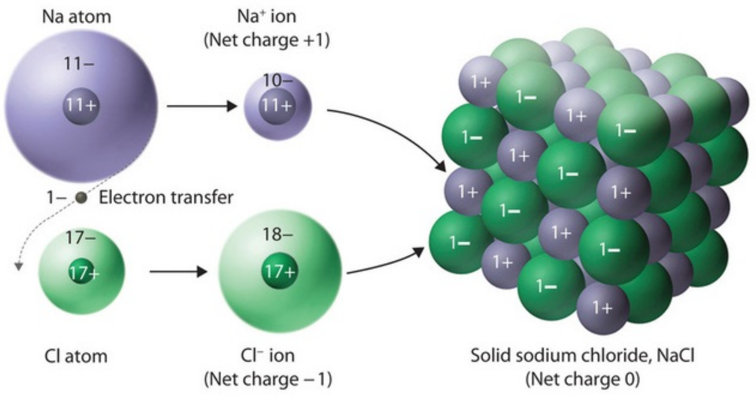


Figure 5.1.7.1: Ionic Bonding. The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

Contributors and Attributions

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5.1.8: Formulas of Ionic Compounds

Learning Objectives

- Write the chemical formula for a simple ionic compound based on the charges of the cations and anions in the compound.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Ionic Compounds Formed From Monoatomic Ions

Consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

$$\mathbf{Na}\cdot \qquad \cdot\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:}$$

$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5$$

For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to obtain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\mathbf{Na}\cdot \curvearrowright \cdot\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:}$$

resulting in two ions—the Na$^+$ ion and the Cl$^-$ ion:

$$\mathbf{Na}\cdot^{+} \qquad \mathbf{:}\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:}^{-}$$

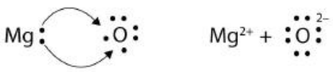
$$[Ne] \qquad [Ne]\,3s^2 3p^6$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na$^+$ and Cl$^-$ ions:

$$\mathbf{Na}\cdot^{+} + \mathbf{:}\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:}^{-} \rightarrow Na^{+}Cl^{-} \;\; or \;\; NaCl$$

where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. As explained previously, the attraction between oppositely charged ions is called an **ionic bond**.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:



Magnesium donates two electrons to oxygen to empty its own orbital and fill oxygens, thus creating Mg2+ and O2-.

The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

$$\mathbf{Mg}^{2+} + \mathbf{:}\underset{\cdot\cdot}{\ddot{\mathbf{O}}}\mathbf{:}^{2-} \qquad Mg^{2+}O^{2-} \; or \; MgO$$

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

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

The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:

Two sodium atoms donate one electron each to oxygen to empty their orbitals and fill oxygen's, thus creating 2 Na+ and O2-.

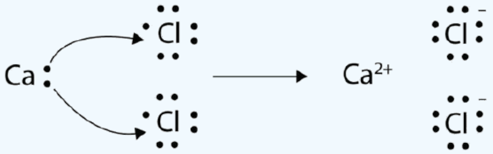
These three ions attract each other to form an overall neutrally charged ionic compound, which we write as Na_2O. The need for the number of electrons lost to be equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is also required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

5.1.8.1 Example

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. We need two Cl atoms to accept the two electrons from one Ca atom. The transfer process is as follows:



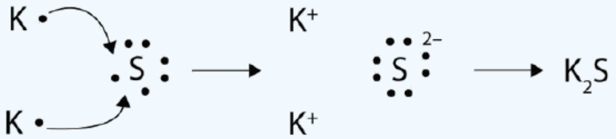
Calcium donates two electrons, one each going to a chlorine. This empties calcium's orbital and fills both of the chlorines'. This creates Ca2+ and two Cl-.

The oppositely charged ions attract one another to make $CaCl_2$.

5.1.8.1 Exercise

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

Answer



Two potassium atoms donate an electron to sulphur to fill sulphur's orbital and empty their own, thus creating two K+ and one S2-. They ionically bond to form K2S.

For compounds in which the ratio of ions is not as obvious, the subscripts in the formula can be obtained by **crossing charges**: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically in Figure 3.3.2.

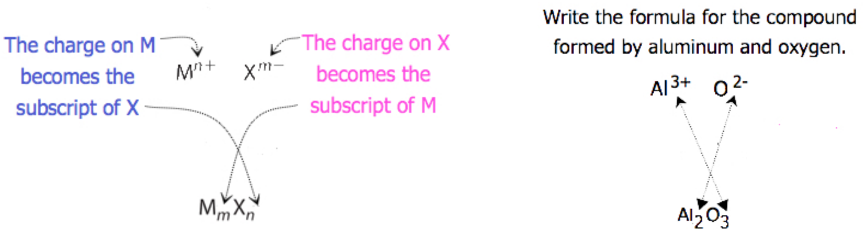


Figure 5.1.8.1: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by Pb^{4+} and O^{2-}. Using the absolute values of the charges on the ions as subscripts gives the formula Pb_2O_4. This simplifies to its correct empirical formula $\mathbf{PbO_2}$. The empirical formula has one Pb^{4+} ion and two O^{2-} ions.

✓ Example 5.1.8.2: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 5.1.8.2) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Figure 5.1.8.2: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

? Exercise 5.1.8.2

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Ionic Compounds Formed From Polyatomic Ions

Many ionic compounds contain polyatomic ions as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $\left(PO_4^{3-}\right)$ groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

✓ Example 5.1.8.3: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

? Exercise 5.1.8.3

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

Answer a:

Mg^{2+} and CO_3^{2-} = $MgCO_3$

Answer b:

Al^{3+} and $C_2H_3O_2^-$ = $Al(C_2H_3O_2)_3$

Formula Unit

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure $5.1.8.3$). As you can see, there are no individual $NaCl$ “particles” in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers or *simplest formula*, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use $NaCl$ (one Na symbol and one Cl symbol) to represent the compound. Thus, $NaCl$ is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that $NaCl$ crystals are composed of individual $NaCl$ units, Figure $5.1.8.3$ shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

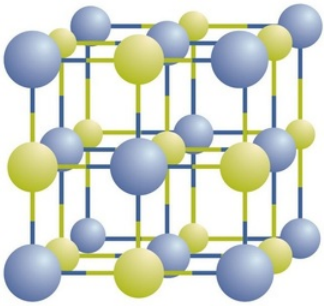


Figure $5.1.8.3$: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

5.1.9: Naming Ionic Compounds

Learning Objectives

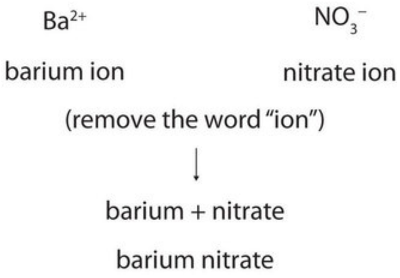
- Write the names for ionic compounds by recognizing and naming the ions in the formula unit.

Ionic compounds are named using the formula unit and by following some important conventions. First, the name of the cation is written *first* followed by the name of the anion. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, charges are *not* included in the name (or the formula). Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. The proper formula for an ionic compound will show how many of each ion is needed to balance the total positive and negative charges; the name does not need to include indication of this ratio.

There are two main types of ionic compound with different naming rules for each; Type I: compounds containing cations of main group elements and Type II: compounds containing cations of variable charge (generally transition metals). Below we will look at examples of each type to learn the rules for naming.

Type I Ionic Compounds

Cations of main group elements do not have variable charges and are the simply named by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\mathrm{Ba(NO_3)_2}$?



The compound's name does not need to indicate that there are two nitrate ions for every barium ion. You must determine the ratio of ions in the formula unit by balancing the positive and negative charges.

Type II Ionic Compounds

Some metals can form cations with variable charges. When naming a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $\mathrm{FeCl_2}$ and $\mathrm{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathrm{Cl^-}$ ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three $\mathrm{Cl^-}$ ions in the formula. These are two different compounds that need two different names. By the *stock system*, the names are iron(II) chloride and iron(III) chloride. If we were to use the stems and suffixes of the *common system*, the names would be ferrous chloride and ferric chloride, respectively.

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 5.1.9.1. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 5.1.9.1: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt

KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

As you practice naming compounds, use Figure 5.1.9.1as a guide.

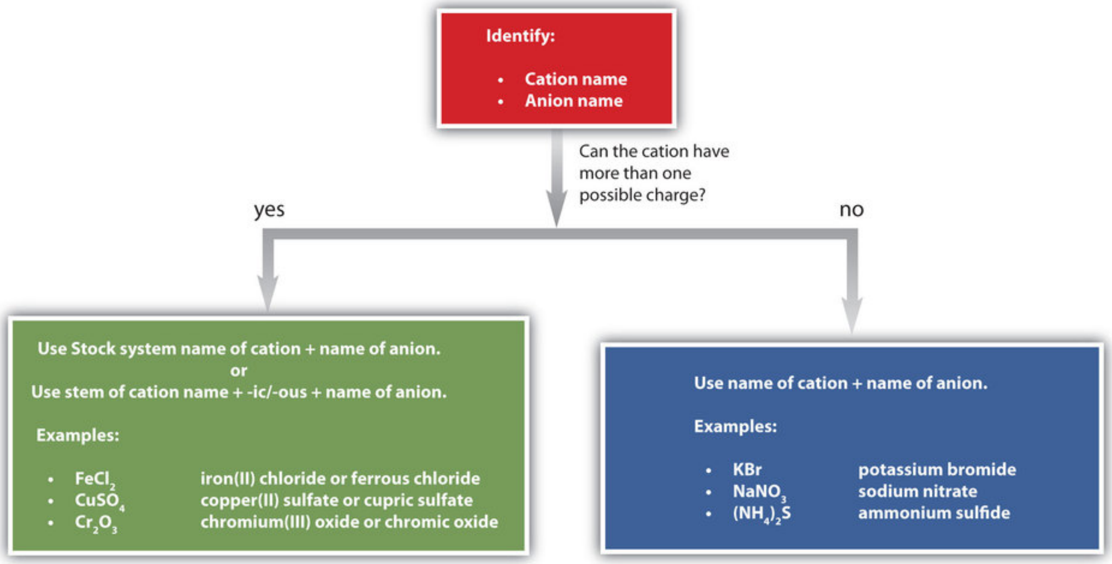


Figure 5.1.9.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound. Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be FeCl2, which is iron(II) chloride of ferrous chloride, CuSO4, which is copper(II) sulfate or cupric sulfate, and Cr2O3, which is chromium(III) oxide or chromic oxide. If the cation can not have more than one possible charge, use the name of the cation and the name of the anion. Examples of this would be KBr, which is potassium bromide, NaNO3, which is sodium nitrate, and (NH4)2S, which is ammonium sulfide.

✓ Example 5.1.9.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $Ca_3(PO_4)_2$
b. $(NH_4)_2Cr_2O_7$

c. KCl
d. CuCl
e. SnF_2

Answer a

calcium phosphate

Answer b

ammonium dichromate (the prefix *di-* is part of the name of the anion)

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 5.1.9.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $ZnBr_2$
b. $Fe(NO_3)_3$
c. Al_2O_3
d. CuF_2
e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

5.1.10: Some Properties of Ionic Compounds

Learning Objectives

- Describe the basic physical properties of ionic compounds.

The figure below shows just a few examples of the color and brilliance of naturally occurring ionic crystals. The regular and orderly arrangement of ions in the crystal lattice is responsible for the various shapes of these crystals, while transition metal ions give rise to the colors.

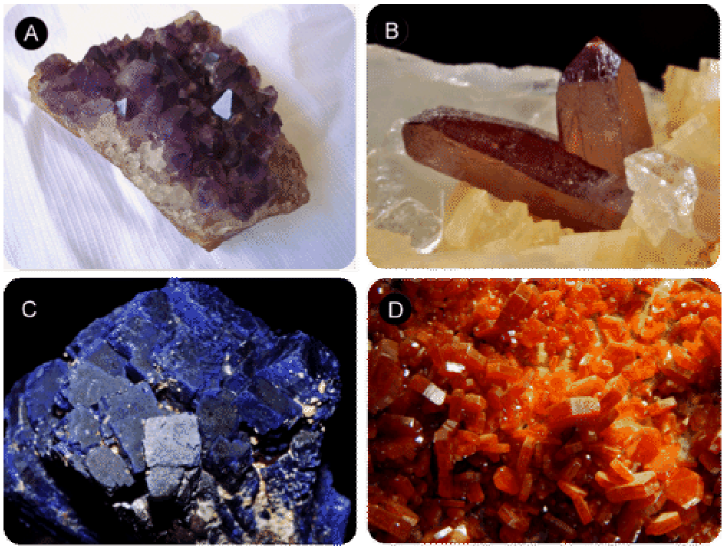


Figure 5.1.10.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz,* SiO_2*, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral,* $Cu_3(CO_3)_2(OH)_2$*. (D) Vanadinite - the primary ore of vanadium,* $Pb_3(VO_4)_3Cl$*.*

Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800 ^{o}C. As a comparison, the molecular compound water melts at 0 °C.

Shattering

Ionic compounds are generally hard, but **brittle.** Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other (see below). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.

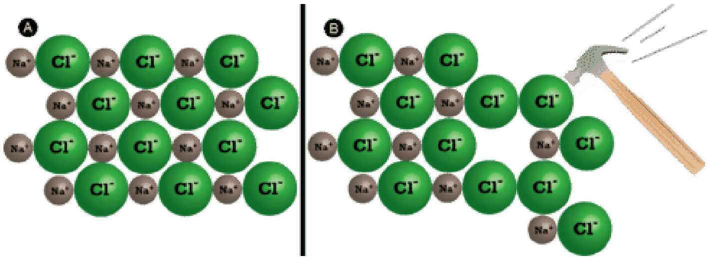
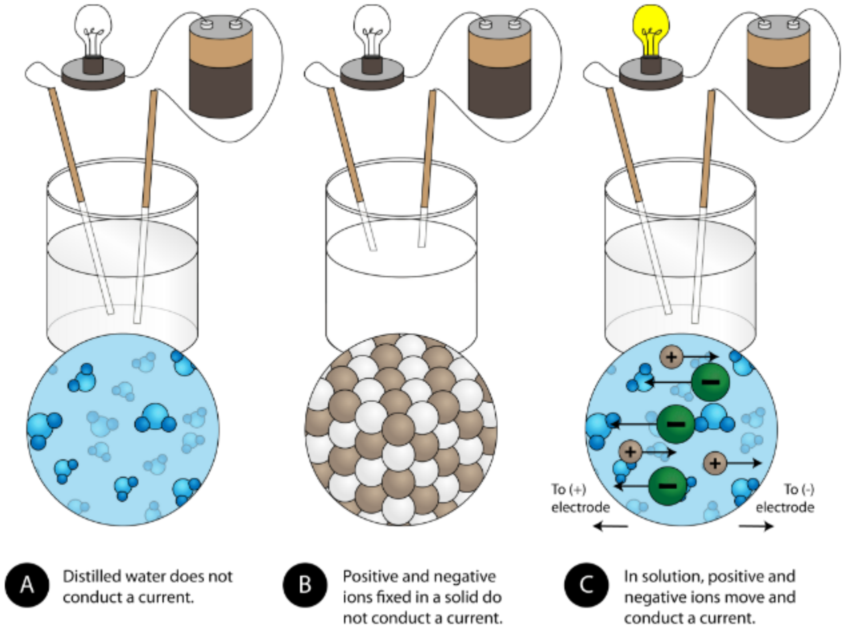


Figure 5.1.10.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

Conductivity

Another characteristic property of ionic compounds is their **electrical conductivity**. The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.



A Distilled water does not conduct a current.

B Positive and negative ions fixed in a solid do not conduct a current.

C In solution, positive and negative ions move and conduct a current.

Figure 5.1.10.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move.

✓ Example 5.1.10.1

Write the dissociation equation of solid NaCl in water.

Solution

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

? Exercise 5.1.10.1

Write the dissociation equation of solid NH_4NO_3 in water.

Answer

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

Key Takeaways

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Ionic compounds dissociate into ions when dissolved in water.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.
- An ionic compound can be identified by its chemical formula: metal + nonmetal or polyatomic ions.

Contributors and Attributions

- CK-12 Foundation by Sharon Bewick, Richard Parsons, Therese Forsythe, Shonna Robinson, and Jean Dupon.

5.1.11: H^+ and OH^- Ions - An Introduction to Acids and Bases

Learning Objectives

- To identify H^+ as an acid and OH^- as a base.

You may have some idea, from your day-to-day experiences, of some chemical substances that are considered acids or bases. Generally, a compound that is sour is recognized as being an acid. Some familiar acids may include citric acid, which is a molecule found in citrus fruits such as lemons and limes, and acetic acid, the molecule that makes up vinegar. Bases, on the other hand, include chemicals such as sodium bicarbonate (baking soda), which is bitter-tasting, and sodium hydroxide, which is found in cleaning substances and is not recommended for ingestion.

More details about acids, bases, and the reactions they undergo will be discussed later in this text. However, because you have just learned about ions and ionic compounds, it is worth pointing out two important ions that are used to identify and distinguish if a substance is acidic or basic; hydrogen ions, H^+, and hydroxide ions, OH^-. In fact, one definition of acids and bases states that an **acid** will produce H^+ when dissolved in water and a **base** will produce a OH^- when dissolved in water.

Ionic compounds that are basic are easily recognized because the hydroxide ion is part of the formula and name. Some common examples are sodium *hydroxide*, $NaOH$, and calcium *hydroxide*, $Ca(OH)_2$. When dissolved in water, sodium hydroxide will split into its constituent ions, sodium ions (Na^+) and hydroxide ions (OH^-) in a 1:1 ratio. However, according to it's chemical formula, calcium hydroxide will produce two hydroxide ions for every one calcium ion, a 1:2 ratio.

Compounds that produce hydrogen ions in water contain one or more hydrogen ions in the chemical formula and usually have special names to help recognize them as acids. Hydrochloric acid (HCl), nitric acid (HNO_3), and carbonic acid (H_2CO_3) are all acids. HCl and HNO_3 each dissolve in water producing a H^+ and an anion (chloride and nitrate respectively). As indicated by the formula for carbonic acid there are two H^+ for every one carbonate ion. The below table lists some common acids. See if you can determine the ratio of H^+ to anions produced when these compounds are dissolved in water.

Table 5.1.11.1 Common Acids and Their Anions

Acid Name	Acid Formula	Anion Name	Anion Formula
acetic acid	CH_3COOH	acetate ion	CH_3COO^-
carbonic acid	H_2CO_3	bicarbonate ion	HCO_3^-
		carbonate ion	CO_3^{2-}
hydrobromic acid	HBr	bromide ion	Br^-
nitric acid	HNO_3	nitrate ion	NO_3^-
nitrous acid	HNO_2	nitrous ion	NO_2^-
phosphoric acid	H_3PO_4	dihydrogen phosphate ion	$H_2PO_4^-$
		hydrogen phosphate ion	HPO_4^{2-}
		phosphate ion	PO_4^{3-}
sulfuric acid	H_2SO_4	hydrogen sulfate ion	HSO_4^-
		sulfate ion	SO_4^{2-}
sulfurous acid	H_2SO_3	hydrogen sulfite ion	HSO_3^-
		sulfite ion	SO_3^{2-}

SECTION OVERVIEW

5.2: Molecular Compounds

5.2.1: Covalent Bonds

Learning Objectives

- Describe how covalent bonds form using the octet rule.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents the lowest potential energy state of two hydrogen atoms and is a balance between several forces: the ***attractions*** between oppositely charged electrons and nuclei, the ***repulsion*** between two negatively charged electrons, and the ***repulsion*** between two positively charged nuclei.

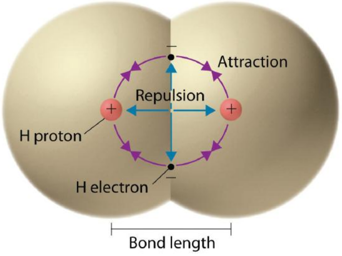


Figure 5.2.1.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 5.2.1.2) shows that energy decreases as two hydrogen atoms move toward each other. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases.

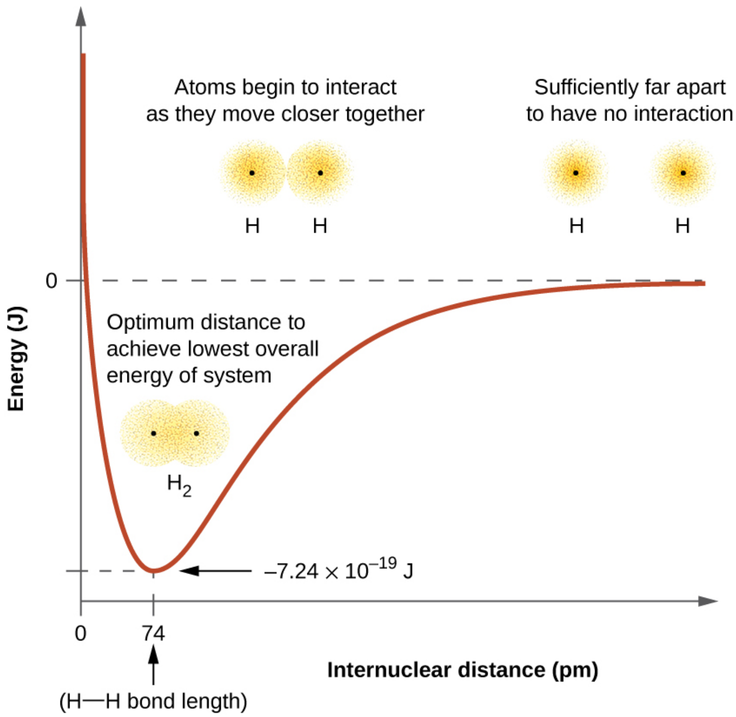


Figure 5.2.1.2: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

Lewis Structures

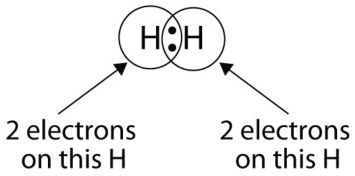
Chemists frequently use Lewis structures to represent covalent bonding in molecular substances. For example, the Lewis symbols of two separate hydrogen atoms are as follows:

H•   •H

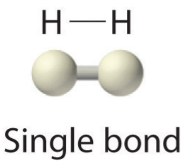
The Lewis structures of two hydrogen atoms sharing electrons looks like this:

H:H

We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom’s valence shell:



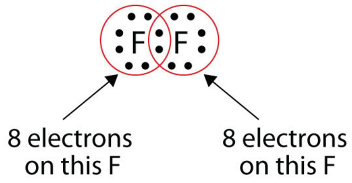
Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. For simplicity’s sake, it is common to represent the covalent bond with a dash, instead of with two dots:



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

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

Note that each F atom has a *complete octet* around it now:



We can also write this using a dash to represent the shared electron pair:

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

Diatomic Molecules

Hydrogen (H_2) and fluorine (F_2) are both described as *diatomic molecules*. These elements and others (see Table 5.2.1.1) exist naturally as molecules rather than as individual atoms. It is important to note that the names of these elements represent molecules and not individual atoms. When describing a single atom rather than a molecule, the word atom is used.

Table 5.2.1.1: Elements That Exist as Diatomic Molecules

Hydrogen (H_2)	Oxygen (O_2)	Nitrogen (N_2)	Fluorine (F_2)
Chlorine (Cl_2)	Bromine (Br_2)	Iodine (I_2)	

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5.2.2: Covalent Bonds and the Periodic Table

Learning Objectives

- Predict the number of covalent bonds formed based on the elements involved and their position on the periodic table.
- Describe the important exceptions to the octet rule.

Diatomic molecules such as hydrogen (H_2), chlorine (Cl_2), fluorine (F_2), etc. containing covalent bonds between two of the same type of atom are only a few examples of the vast number of molecules that can form. Two different atoms can also share electrons and form covalent bonds. For example, water, (H_2O), has two covalent bonds between a single oxygen atom and two hydrogen atoms. Ammonia, (NH_3, is a central nitrogen atom bonded to three hydrogen atoms. Methane, (CH_4, is a single carbon atom covalently bonded to four hydrogen atoms. In these examples the central atoms form different numbers of bonds to hydrogen atoms in order to complete their valence subshell and form octets.

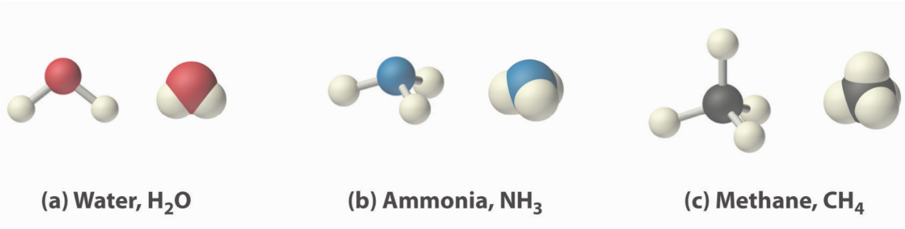
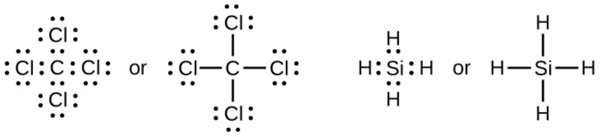


Figure 5.2.2.4: 3D molecule examples. From left to right: water molecule, ammonia molecule, and methane molecule

How Many Covalent Bonds Are Formed?

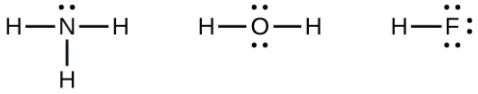
The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride

silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia

Water

hydrogen fluoride

The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

Table showing 4 different atoms, each of their number of bonds, and each of their number of lone pairs.

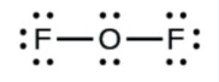
Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14)	4	0

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Nitrogen (Group 15)	3	1
Oxygen (Group 16)	2	2
Fluorine (Group 17)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the *duet rule*. Hydrogen only needs to form one bond to complete a duet of electrons. This is the reason why H is always a terminal atom and never a central atom.

✓ Example 5.2.2.1

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?

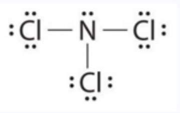


Solution

Yes. F (group 7A) forms one bond and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

? Exercise 5.2.2.1

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

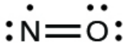
Octet Rule Exceptions

As important and useful as the octet rule is in chemical bonding, there are many covalent molecules with central atoms that do not have eight electrons in their Lewis structures. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient (diminished octet) molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Expanded octet (hypervalent) molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron molecules

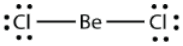
Although they are few, some stable compounds, often called *free radicals*, have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable, odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO, a compound produced in internal combustion engines when oxygen and nitrogen react at high temperatures, is as follows:



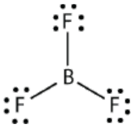
As you can see, the nitrogen and oxygen share four electrons between them. The oxygen atom has an octet of electrons but the nitrogen atom has only seven valence electrons, two electrons in the double bond, one lone pair, and one additional lone electron. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules

These stable compounds have less than eight electrons around an atom in the molecule, i.e. they have less than an octet. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:

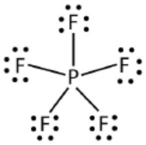


Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:

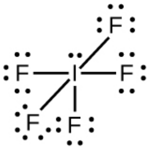


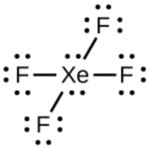
Expanded Octet Molecules

Elements in the second period of the periodic table (n = 2) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods (n ≥ 3) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements have expanded octets and are sometimes called hypervalent molecules. Phosphorous pentachloride shares five pairs of electrons for a total of ten electrons in the valence shell.



In some expanded octet molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:





Example 5.2.2.2

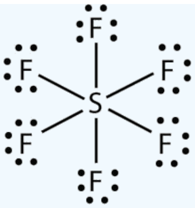
Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

a. ClO
b. SF_6

Solution

1. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:

2. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:

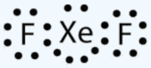


Exercise 5.2.2.2: Xenon Difluoride

Identify the violation to the octet rule in $\mathrm{XeF_2}$ by drawing a Lewis electron dot diagram.

Answer

The Xe atom has an expanded valence shell with more than eight electrons around it.



Concept Review Exercises

1. How is a covalent bond formed between two atoms?
2. How does covalent bonding allow atoms in group 6A to satisfy the octet rule?

Answers

1. Covalent bonds are formed by two atoms sharing electrons.
2. The atoms in group 6A make two covalent bonds.

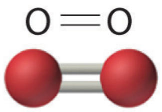
5.2.3: Multiple Covalent Bonds

Learning Objectives

- Identify when a multiple bond (double or triple) is needed to complete an octet.

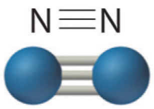
The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***



Double bond

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

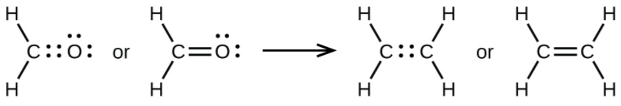


Triple bond

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

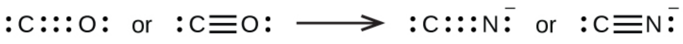
In addition to nitrogen and oxygen, carbon will also commonly form multiple bonds to complete valence octets. Additional examples involving these three atoms are shown below.

A double bond is formed between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

A triple bond is formed between carbon and oxygen in carbon monoxide (CO) and between carbon and nitrogen in the cyanide ion (CN^{-}):



carbon monoxide cyanide ion

Example 5.2.3.1: Writing Lewis Structures

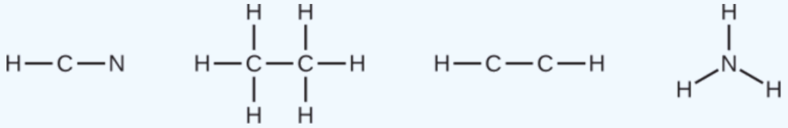
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

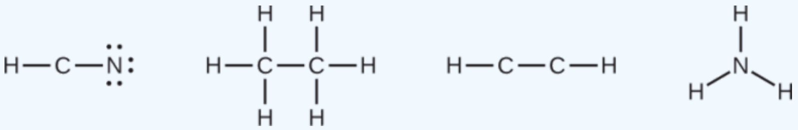
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

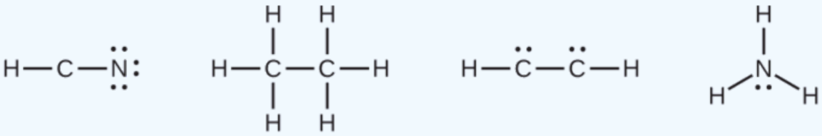


Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain
- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

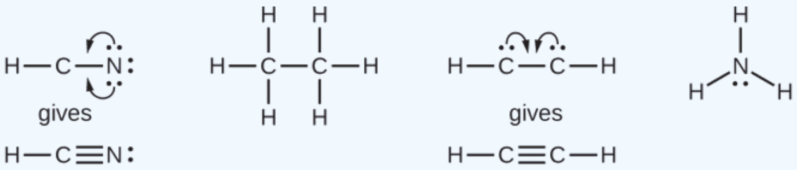
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

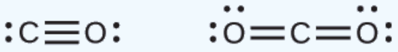
- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



Exercise 5.2.3.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



5.2.4: Characteristics of Molecular Compounds

Learning Objectives

- Compare the properties of ionic and molecular compounds.

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* (discussed further in a later chapter) 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 5.2.4.1: Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	Metal and nonmetal	Nonmetals only
Bonding	Ionic - transfer of electron(s) between atoms	Covalent - sharing of pair(s) of electrons between atoms
Representative unit	Formula unit	Molecule
Physical state at room temperature	Solid	Gas, liquid, or solid
Water solubility	Usually high	Variable
Melting and boiling temperatures	Generally high	Generally low
Electrical conductivity	Good when molten or in solution	Poor

In summary, covalent compounds are softer, have lower boiling and melting points, are more flammable, are less soluble in water and do not conduct electricity compared to ionic compounds. The individual melting and boiling points, solubility and other physical properties of molecular compounds depend on molecular polarity.

5.2.5: Molecular Formulas and Lewis Structures

Learning Objectives

- Understand the different ways to represent molecules.

There are many "universal languages" in the world. Musicians of every culture recognize music embodied in a series of notes on a staff. This passage from a Bach cello suite could be played by any trained musician from any country, because there is an agreement as to what the symbols on the page mean. In the same way, molecules are represented using symbols and a language that all chemists agree upon.

Figure $5.2.5.1$ (Credit: J. S. Bach; Source: http://commons.wikimedia.org/wiki/File:Bach_cello_harmony.JPG(opens in new window); License: Public Domain)

Molecular Formulas

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

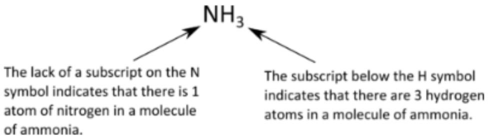
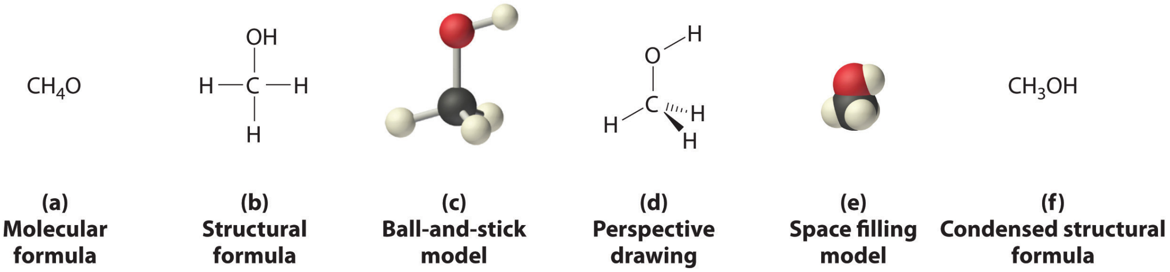


Figure $5.2.5.2$: The molecular formula for ammonia. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Note from the example that there are some standard rules to follow in writing molecular formulas. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write $\mathrm{N_3H}$ for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

Although it is useful for describing a molecule, the molecular formula does not tell us anything about the shape of the molecule, where the different atoms are, or what kinds of bonds are formed. **Structural formulas** are much more useful to communicate more detailed information about a molecule because they show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

Figure $5.2.5.3$ shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (Figure $5.2.5.3a$) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (Figure $5.2.5.3b$) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure $5.2.5.3$) and the perspective drawing (Figure $5.2.5.3d$) show the three-dimensional structure of the molecule. The latter (also called a wedge-and-dash representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure $5.2.5.3$) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. In addition, in a space-filling model, atoms at the “front” of the molecule may obscure atoms at the “back.”



(a) Molecular formula **(b) Structural formula** **(c) Ball-and-stick model** **(d) Perspective drawing** **(e) Space filling model** **(f) Condensed structural formula**

Figure 5.2.5.3: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a condensed structural formula (part (f) in Figure 5.2.5.3), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which indicates that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

✓ Example 5.2.5.1: Molecular Formulas

Write the molecular formula for each compound. The condensed structural formula is given.

a. Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl.
b. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
c. Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(CH_3)_3N$.

Given: condensed structural formula

Asked for: molecular formula

Strategy:

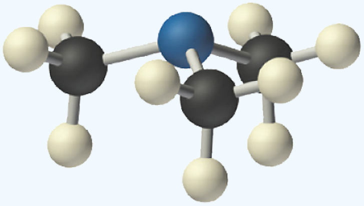
A. Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.
B. As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

Solution:

The molecular formula lists the elements in the molecule and the number of atoms of each.

a. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
b. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.

c. **A** The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula C_3H_9N.

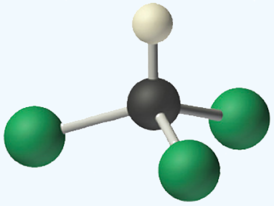


Trimethylamine

Exercise 5.2.5.1: Molecular Formulas

Write the molecular formula for each molecule.

a. Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms. Its condensed structural formula is $CHCl_3$.
b. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is H_2NNH_2.
c. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is H2NCH2CH2CH2CH2NH2. This is often written as $H_2N(CH_2)_4NH_2$ to indicate that there are four CH2 fragments linked together.



Chloroform

Answer a

$CHCl_3$

Answer b

N_2H_4

Answer c

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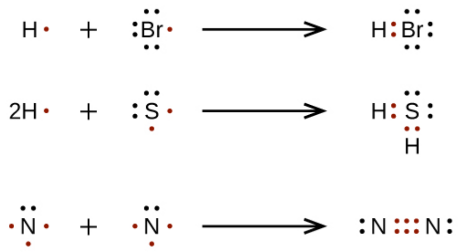
5.2.6: Drawing Lewis Structures

Learning Objectives

- Draw Lewis structures for molecules.

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



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

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:

Because this structure gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:

Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

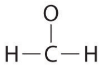
Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for a molecular ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:

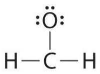
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

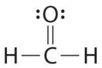
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

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

✓ Example 5.2.6.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

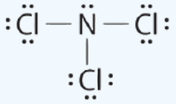
Asked for: Lewis electron structures

Strategy:

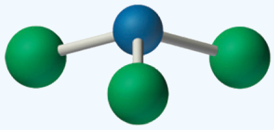
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

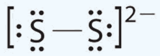


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



Nitrogen trichloride

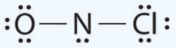
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



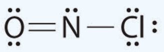
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:

O—N—Cl

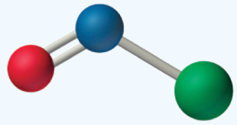
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



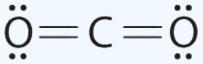
Nitrosyl chloride

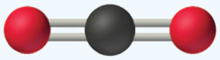
? Exercise 5.2.6.1

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

Answer

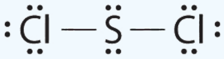
1.



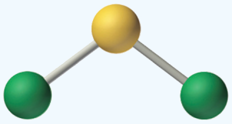


Carbon dioxide

2.



Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.



Sulfur dichloride

5.2.7: The Shapes of Molecules

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

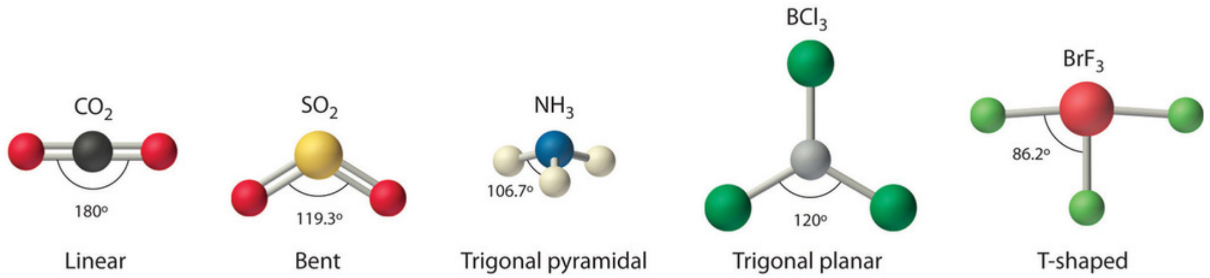


Figure 5.2.7.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form **electron groups** (regions of electron density), which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 5.2.7.1.

It is important to note that electron group geometry around a central atom is *not* the same thing as its molecular structure. Electron group geometries describe ***all*** regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms* alone, not including the lone pair electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron group geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure** (or molecular shape). The electron group geometries will be the *same* as the molecular structures when there are no lone electron pairs around the central atom, but they will be *different* when there are lone pairs present on the central atom.

Predicting Electron Group Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine electron group geometry and molecular structures (molecular shape):

1. Draw the Lewis structure of the molecule or polyatomic ion.

2. Count the number of electron groups or regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one electron group.
3. Determine the electron group geometry by placing the groups as far apart as possible.
4. Determine the molecular structure (looking at the bonded groups only).

Table 5.2.7.1summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 5.2.7.1: Summary of Electron Group Geometries and Molecular Structures

Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Group Geometry	Molecular Structure
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent 120°
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent 109°

Two Electron Groups

Any molecule with only two atoms is **linear**. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible, which is 180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular structure is linear. Examples include BeH_2 and CO_2:

Figure 5.2.7.2: Beryllium hydride and carbon dioxide bonding.

Three Electron Groups

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle, 120° apart and in a plane. The shape of such molecules is **trigonal planar**. An example is BF_3:

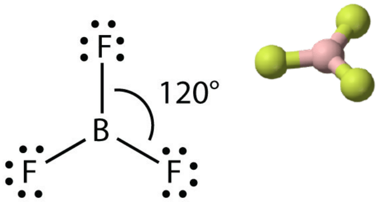


Figure 5.2.7.3: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

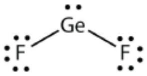


Figure 5.2.7.4: Germanium difluoride bonding.

From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This molecular structure is called **bent 120°** or angular.

Four Electron Groups

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron with bond angles of approximately 109.5°. If there are four atoms attached to these electron groups, then the molecular structure is also **tetrahedral**. Methane (CH_4) is an example.

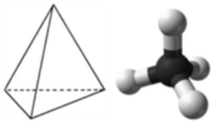


Figure 5.2.7.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

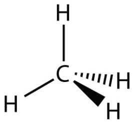


Figure 5.2.7.6: Methane bonding. (CK12 Licence)

NH_3 is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

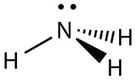


Figure 5.2.7.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a *tetrahedron*, from a molecular geometry perspective, the shape of NH_3 is **trigonal pyramidal**.

H_2O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.

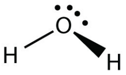


Figure 5.2.7.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is **bent 109°** or angular. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Shapes of Molecules with Double or Triple Bonds

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 5.2.7.9

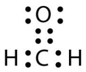


Figure 5.2.7.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a *trigonal planar shape*.

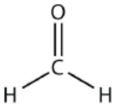


Figure 5.2.7.10: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

✓ Example 5.2.7.1

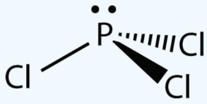
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

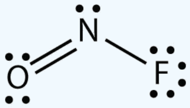
The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

? Exercise 5.2.7.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

? Exercise 5.2.7.2

Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

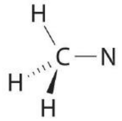
Answer

Trigonal planar about both central C atoms.

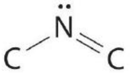
Molecules With Multiple Central Atoms

The VSEPR model can be used to predict the structure of somewhat more complex molecules with more than one central atom by using VSEPR as described above for each central atom individually. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin.

Start by looking at the electron groups around the first carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. There are four groups or electrons or four bonds around the carbon. We can therefore predict the CH_3–N portion of the molecule to be roughly *tetrahedral*, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron groups. Thus according to the VSEPR model, the C–N=C fragment should be *bent* with an angle ~120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

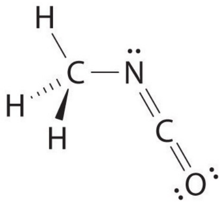


Figure 5.2.7.11). The Lewis Structure of Methyl Isocyanate

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

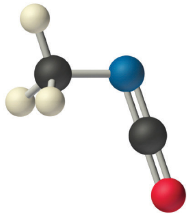


Figure 5.2.7.12: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

✓ Example 5.2.7.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 5.2.7.3to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise 5.2.7.3

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

5.2.8: Polar Covalent Bonds and Electronegativity

Learning Objectives

- Describe electronegativity and polarity.
- Use electronegativity values to predict bond polarity.

Our discussions of bonding thus far have focused on two types, ionic and covalent. In ionic bonds, like $NaCl$, electrons are *transferred*; the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom, and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions. In covalent bonding, unpaired electrons from individual atoms are *shared* in order to fill the valence shell of each atom. When a covalent bond is formed between the same type of atoms, such as Cl_2, the electrons are *shared equally* between the two. However, when a covalent bond is formed between different types of atoms, the electrons are not necessarily shared equally. In these compounds their bond character falls *between* the two extremes: transferred and shared equally.

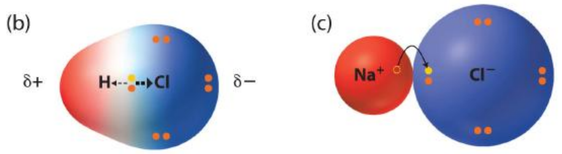
Bond Polarity

As demonstrated below, **bond polarity** is a useful concept for describing the sharing of electrons between atoms, within a covalent bond:

- A **nonpolar covalent bond** (Figure $5.2.8.1a$) is one in which the electrons are shared *equally* between two atoms.
- A **polar covalent bond** (Figure $5.2.8.1b$) is one in which one atom has a greater attraction for the electrons than the other atom.
- If the relative attraction of an atom for electrons is great enough, then the bond is an **ionic bond (**Figure $5.2.8.1c$).

Electron density in a polar bond is distributed unevenly and is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the shaded area around Cl in Figure $5.2.8.1b$ is much larger than it is around H. This imbalance in electron density results in a buildup of *partial negative charge* (designated as δ−) on one side of the bond (Cl) and a *partial positive charge* (designated δ+) on the other side of the bond (H).

Nonpolar covalent bond
Bonding electrons shared equally between two atoms.
No charges on atoms.



Polar covalent bond
Bonding electrons shared unequally between two atoms.
Partial charges on atoms.

Ionic bond
Complete transfer of one or more valence electrons.
Full charges on resulting ions.

Figure $5.2.8.1$: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use electronegativity, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

Electronegativity

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity**, defined as the *relative ability* of an atom to attract electrons to itself in a chemical compound. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

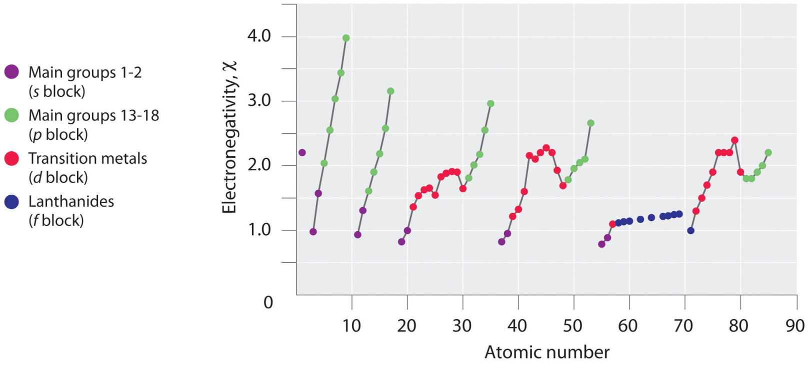


Figure 5.2.8.2: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations (trends) in Pauling’s electronegativity values are illustrated in Figures 5.2.8.2and 5.2.8.3. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine is the most electronegative element and cesium is the least electronegative nonradioactive element. Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl, and N, S, and Br).

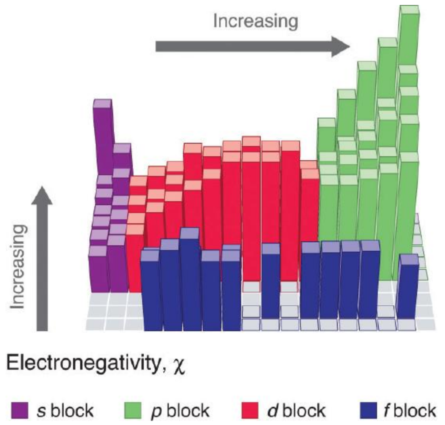
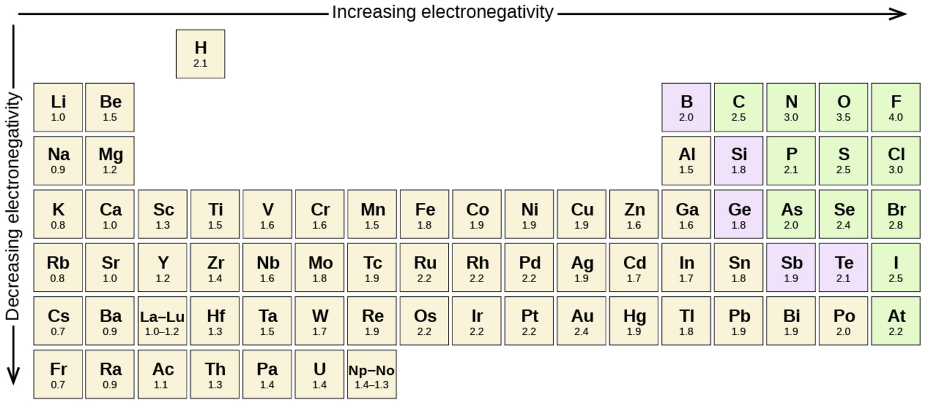


Figure 5.2.8.3: Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

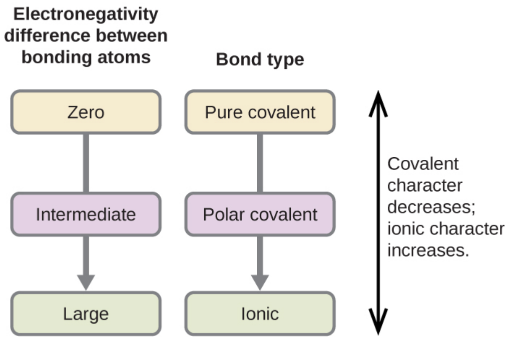
The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond. Although there are no hard and fast rules, the general rule, (see Figure 5.2.8.5), is if the difference in electronegativities is less than about 0.4, the bond is considered nonpolar; if the difference is greater than 0.4, the bond is considered polar. If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.



		H 2.1														
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La–Lu 1.0–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np–No 1.4–1.3										

Figure 5.2.8.4 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 5.2.8.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Example 5.2.8.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

a. C and H
b. H and H
c. Na and Cl
d. O and H

Solution

a. Carbon has an electronegativity of 2.5, while the value for hydrogen is 2.1. The difference is 0.4, which is rather small. The C–H bond is therefore considered nonpolar.
b. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
c. Sodium's electronegativity is 0.9, while chlorine's is 3.0. The difference is 2.1, which is rather high, and so sodium and chlorine form an ionic compound.
d. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. We would expect a very polar bond. The sharing of electrons between O and H is unequal with the electrons more strongly drawn towards O.

Exercise 5.2.8.1

Describe the electronegativity (EN) difference between each pair of atoms and the resulting polarity (or bond type).

a. C and O
b. K and Br
c. N and N
d. Cs and F

Answer a:

The EN difference is 1.0 , hence polar. The sharing of electrons between C and O is unequal with the electrons more strongly drawn towards O.

Answer b:

The EN difference is greater than 1.8, hence ionic.

Answer c:

Identical atoms have zero EN difference, hence nonpolar.

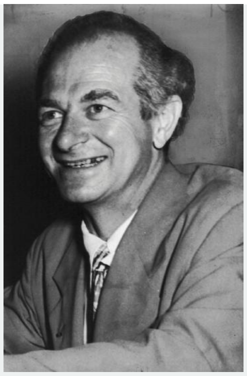
Answer d:

The EN difference is greater than 1.8, hence ionic.

Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–94) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.

5.2.9: Polar Molecules

Learning Objectives

- Recognize bond characteristics of covalent compounds: bond length and bond polarity.
- Use electronegativity values to predict bond polarity.

If there is only one bond in the molecule, the bond polarity determines the *molecular polarity*. Any diatomic molecule in which the two atoms are the same element must be a nonpolar molecule. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule where one end of the molecule is slightly positive, while the other end is slightly negative. 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. Hence, a molecule with two poles has a **dipole moment**.

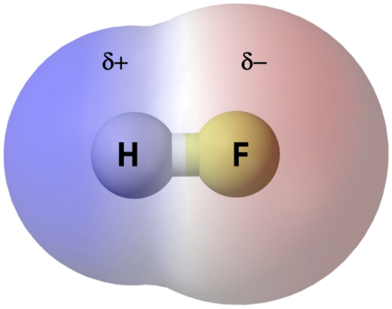


Figure 5.2.9.1: A molecular dipole results from the unequal distribution of electron density throughout a molecule. The H, with less electron density is partially positive and the F, with more electron density is partially negative. (Figure modified from: Wikipedia [en.Wikipedia.org])

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 with carbon in the center and two oxygens at the terminal ends. 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 pointing in opposite directions, they *cancel out* and the overall molecular polarity of CO_2 is zero (no net dipole), therefore CO_2 is a *nonpolar molecule*.

Water has a bent molecular structure because it has four electron groups, two bonded groups and two lone electron groups on the central oxygen atom. The individual O–H bond dipoles point from the slightly positive H atoms toward the more electronegative O atom. Because of the bent shape, the dipoles, which are equal in strength, both point towards the oxygen atom and will not cancel each other out, therefore, the water molecule is polar. In the figure below, you can see that the oxygen end of the molecule is slightly negative and the hydrogen side is slightly positive, there is a separation of charge throughout the whole molecule, a **net dipole** (shown in blue) that points upward.

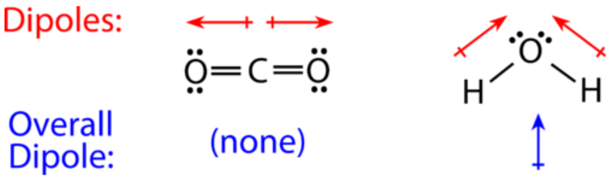


Figure 5.2.9.2: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. In contrast, water is polar because the OH bond dipole moments do not cancel out. There is a net separation of charge or overall dipole moment.

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.

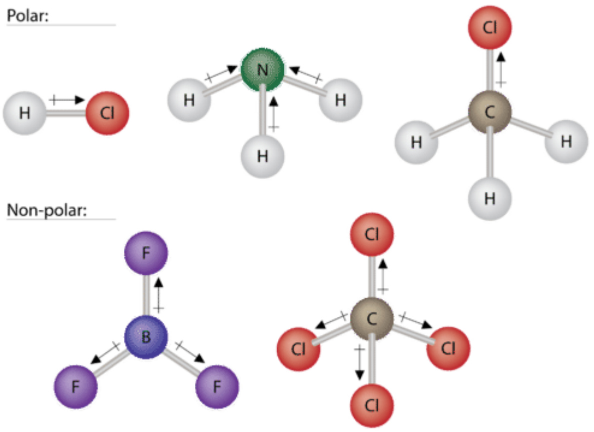


Figure 5.2.9.3: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment do not cancel.

Steps to Identify Polar Molecules

1. Draw the Lewis structure.
2. Figure out the geometry (using VSEPR theory).
3. Visualize or draw the geometry.
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it).
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 5.2.9.4). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

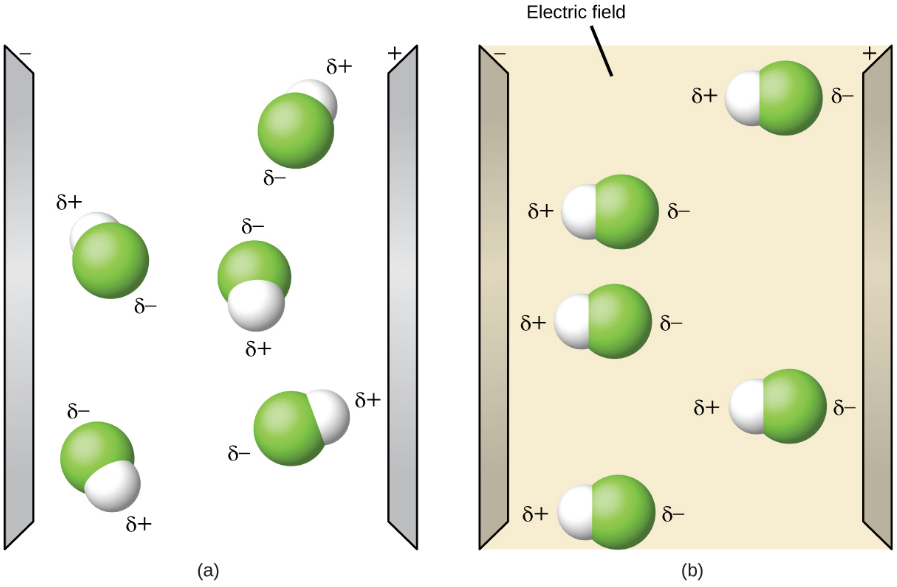


Figure 5.2.9.4: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

✓ Example $5.2.9.1$: Polarity Simulations

Open the molecule polarity simulation (above) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

? Exercise $5.2.9.1$

Determine the partial charges that will give the largest possible bond dipoles.

Answer

> The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

5.2.10: Naming Binary Molecular Compounds

Learning Objectives

- Name binary molecular compounds.

Naming *binary* (two-element) covalent compounds is very similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix -*ide*. Unlike for ionic compounds, molecular compounds can be formed using the same elements in different ratios. Therefore, it is important to indicate the number of each type of atom, using a system of numerical prefixes, listed in Table 5.2.10.1 Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 5.2.10.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-
*This prefix is not used for the first element's name.	

Let us practice by naming the compound whose molecular formula is CCl_4. The name begins with the name of the first element carbon. The second element, chlor*ine*, becomes chlor*ide*, and we attach the correct numerical prefix ("tetra-") to indicate that the molecule contains four chlorine atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

✓ Example 5.2.10.1

Write the molecular formula for each compound.

a. chlorine trifluoride
b. phosphorus pentachloride
c. sulfur dioxide
d. dinitrogen pentoxide

Solution

If there is no numerical prefix on the first element's name, we can assume that there is only one atom of that element in a molecule.

a. ClF_3
b. PCl_5
c. SO_2
d. N_2O_5 (The *di-* prefix on nitrogen indicates that two nitrogen atoms are present.)

? Exercise $5.2.10.1$

Write the molecular formula for each compound.

a. nitrogen dioxide
b. dioxygen difluoride
c. sulfur hexafluoride
d. selenium monoxide

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

> Because it is so unreactive, sulfur hexafluoride is used as a spark suppressant in electrical devices such as transformers.

✓ Example $5.2.10.2$

Write the name for each compound.

a. BrF_5
b. S_2F_2
c. CO

Solution

a. bromine pentafluoride
b. disulfur difluoride
c. carbon monoxide

? Exercise $5.2.10.2$

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- H_2O: water
- NH_3: ammonia
- CH_4: methane

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce later.

5.3: Chemical Bonding (Worksheet)

Name: ______________________________

Section: ______________________________

Student ID#:__________________________

Work in groups on these problems. You should try to answer the questions without referring to your textbook. If you get stuck, try asking another group for help.

Learning Objectives

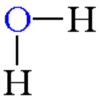
1. Be able to define covalent bonds, polar covalent bonds, ionic bonds, electronegativity, dipoles, molecular formula, structural formula and electron-dot formula.
2. Be able to recognize whether the type of bond between two atoms is covalent, polar covalent or ionic.
3. Be able to draw electron-dot formulas for simple molecules.

Bond Classifications

Chemical bonds are the attractive forces that hold atoms together in the form of compounds. A chemical bond is formed when electrons are shared between two atoms. There are three types of bonds: **covalent bonds**, **polar covalent bonds** and **ionic bonds**. The simplest example of bonding is demonstrated by the H_2 molecule. We can see that each hydrogen atom has a single electron from the periodic table. If two hydrogen atoms come together to form a bond, then each hydrogen atom effectively has a share in both electrons and thus each resembles an inert gas structure. The two electrons that are shared are considered to be a chemical bond and can be represented with either two dots or a single dash between the two bonded atoms.

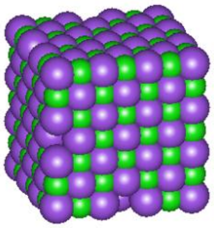
Covalent Bond: A *covalent bond* is formed when there is an equal sharing of electrons between two atoms. The atoms forming a covalent bond must have relatively equal attraction for the electrons. The bonds between the carbon atom and the hydrogen atoms in the compound methane CH_4 are examples of covalent bonds between two different elements.

Polar covalent bond: If the atoms differ in their attraction for electrons, a polar-covalent bond will be formed. Water is an example of a molecule with this type of bond.



The attraction of electrons to the nucleus of an atom is a very important property of atoms and is called **electronegativity**. The difference in electronegativity between bonded atoms determines the **bond polarity**, which is determined by the relative difference in electronegativity between two atoms that are joined together by a chemical bond. A dipole results from an unequal distribution of the electron pair in the bond between the atoms.

Ionic bonds: An ionic bond is formed when an electron is essentially transferred from one atom of a pair to the other creating ions. Sodium chloride is an example of a compound with this type of bond. These compounds exist as a crystal lattice with all the ions stacked in definite patterns. The following picture is a representation of a cubic crystal of sodium chloride. The chloride ions are represented by the purple spheres.



Remember that a cation is a positively charged atom or molecule (one that has lost one or more electrons) and that an anion is a negatively charged atom or molecule (one that has gained one or more electrons). The ions are held together by electrostatic attractions. Ionic compounds have high melting points and many are soluble in water.

Most compounds that contain metals are ionic. For the purpose of this course, you may assume that all compounds that contain metals are ionic. If a compound contains the ammonium ion, it will be ionic. That is why the compound ammonium nitrate is written as NH_4NO_3 rather than $N_2H_4O_3$. This alerts people to the fact that the compound contains the ammonium group and the nitrate group.

Methods of Showing Formulas of Compounds

- **Molecular formulas** show only the type and number of atoms in a molecule.
- **Structural formulas** show the atoms in their correct placement in the molecule.
- **Electron-dot formulas** are similar to structural formulas but also include all of the non-bonding outer electrons. Knowledge of electron placement aids in understanding how molecules and elements react with one another.

Drawing Electron-Dot Formulas

Step 1: Sum up the total number of valence electrons for the elements in the molecule. If the molecule is charged, subtract one electron for each positive charge or add one electron for each negative charge.

Step 2: Write the structure for the molecule with a pair of electrons (or a dash) between each atom. Groups of atoms will usually have the less electronegative atom surrounded by atoms having greater electronegativity. Never place a hydrogen atom in the center since it can only form one bond. Think about the valence of each atom and make sure that these valences are not exceeded except in the case of ions. Ions always have more or less bonds than the normal uncharged atom. The common valence or number of bonds formed for some common atoms are:

- H = 1
- O and S = 2
- N = 3
- C = 4
- F, Cl, Br and I = 1

Step 3: Place electrons around the outer atoms to fill their outer shells. Most atoms require eight electrons (the octet rule) so they will resemble an inert gas. Elements in Group I to Group 13 often do not follow the octet rule and have less than eight electrons in the final formula.

Step 4: Subtract the number of electrons used so far from the total calculated in *Step 1* and place these remaining electrons on the central atom or atoms.

Step 5: If the central atom ends up with less than 8 electrons, then it probably forms a multiple bond with an adjacent outer atom.

Example 1: Methane CH_4

The first electron-dot formula we shall draw will be methane, CH_4.

Step 1: The first thing that you must do is to determine the number of electrons available for the formula.

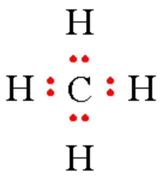
- Hydrogen is a Group 1 element and thus has 1 valance electron. Since there are 4 hydrogen atoms, the total for hydrogen will be 4 electrons.
- Carbon is in Group 14 element thus has 4 outer electrons (remember that we don't use the atomic number for electron-dot formulas).

  The total number of electrons for all atoms is 8.

Step 2: The next step is to determine which atom will be in the center of the molecule. Hydrogen atoms are only able to form one bond to other atoms so we need to put the carbon atom in the center.

Step 3: The next step requires drawing a "C" and "H" and place 2 electrons between these atoms.

Step 4: All you have to do now is draw all of the other hydrogen atoms around the carbon atom and place 2 electrons between these hydrogen atoms and the carbon atom. This gives you a total of 8 electrons and you have drawn the electron-dot formula for methane.



Step 5: A full octet. No further effort needed.

Example 2: Water H_2O

Then let's try a compound that has non-bonding electron pairs: water.

Step 1: The first thing that you must do is to determine the number of electrons available for the formula.

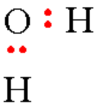
- Hydrogen is a Group 1 element and thus has 1 valance electron. Since there are 2 hydrogen atoms, the total for hydrogen will be 2 electrons.
- Oxygen is a Group 16 element thus has 6 outer electrons (remember that we don't use the atomic number for electron-dot formulas).

The total number of electrons for all atoms is 8.

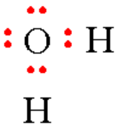
Step 2: The next step is to determine which atom will be in the center of the molecule. Hydrogen atoms are only able to form one bond to other atoms so we need to put the oxygen atom in the center.

Step 3: The next thing that you must do is to draw an "O" and "H" and place 2 electrons between these atoms.

Step 4: Now repeat this with the second "H". Don't worry about where these atoms are positioned around the oxygen atom, it does not matter for this representation.



Step 5: Now all you have to do is place the remaining 4 electrons on the oxygen atom. The hydrogen atoms can only share in 2 electrons so don't put more electrons around them. This gives you a total of 8 electrons and you have drawn the electron-dot formula for water.



Example 3: Hydroxide Ion

The next example will be an ion with a negative charge, the hydroxide ion, HO^-.

Step 1: The first thing that you must do is to determine the number of electrons available for the formula?

- Hydrogen is is a Group 1 element and thus has 1 electron.
- Oxygen is a Group 16 element and thus has 6 outer electrons.
- We must add one electron for the negative charge.

The total number of electrons for both atoms including the extra electron for the negative charge is 8.

Step 2: Draw the hydrogen atom next to the oxygen atom and place a pair of electrons between the atoms.

Step 3: The last thing needed to complete the formula is to place the remaining 6 electrons around the oxygen atom.

Example 4: Ammonium Ion

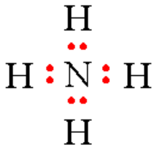
Now let's see what happens when we have a positive charge and draw the ammonium ion, NH_4^+.

Step 1: The first thing that you must do is to determine the number of electrons available for the formula?

- Hydrogen is a Group 1 element and thus has 1 electron. Since there are 4 hydrogen atoms, we have 4 electrons.
- Nitrogen is is a Group 15 element and thus has 5 outer electrons.
- We must subtract one electron for the positive charge.

The total number of electrons for all atoms including the loss of an electron for the positive charge is 8.

Steps 2-5: Draw the nitrogen atom in the center and place the 4 hydrogen atoms around it. Draw a pair of electrons between each pair. This actually finishes the formula. Notice that this structure looks exactly like the structure for methane except that the center atom is a nitrogen atom. When two structures have identical electron-dot formulas, they are considered to be *isoelectronic*.



Step 5:

Example 5: Molecular Oxygen

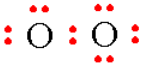
Finally, let's draw a compound that requires multiple bonds and draw the formula for oxygen, O2.

Step 1: The first thing that you must do is to determine the number of electrons available for the formula?

- Oxygen is a Group 16 element and thus has 6 outer electrons...since there are 2 oxygen atoms, there will be a total of 12 electrons.

Step 2: Draw the 2 oxygen atoms with a pair of electrons between them.

Step 3: The next thing that you must do is to draw the remaining electrons in pairs around each of the oxygen atoms giving neither atom more than 8 total electrons.



Step 4: The oxygen atom on the right has 8 electrons but the oxygen atom on the left has only 6 electrons. The only way to correct this problem is to create a multiple bond between the oxygen atoms. Take a pair of electrons from the oxygen atom on the right and place this pair between the 2 atoms.

Q1

a. Define a covalent bond.
b. Define a polar-covalent bond.
c. Define an ionic bond.

Q2

a. Define electronegativity. Why does electronegativity increase going from left to right in a row in the periodic table?
b. Why does electronegativity increase going from bottom to top in a column in the periodic table?

Q3

Describe the type of bond represented by the dash for each of the following compounds using the definitions in Q1. Consider only the atoms to which the dash is directly connected.

- H–H
- H–CH_3
- H–NH_2
- Na–ONa
- Na–Br
- K–OH
- H–OH
- H–Br
- F–CH_3

Q4

Draw the electron-dot formulas for the following compounds or ions.

- HF
- H_2S
- F^-
- Br^+
- N_2
- HCN
- NC^-

CHAPTER OVERVIEW

6: Chemical Reactions

6.1: Chemical Equations

Learning Objectives

- Define *chemical reaction*.
- Understand the Law of Conservation of Matter

Water (H_2O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H_2) and elemental oxygen (O_2) and let them react to make water. The statement

"hydrogen and oxygen react to make water"

is one way to represent that process, which is called a chemical reaction. Figure $6.1.1$ shows a rather dramatic example of this very reaction.

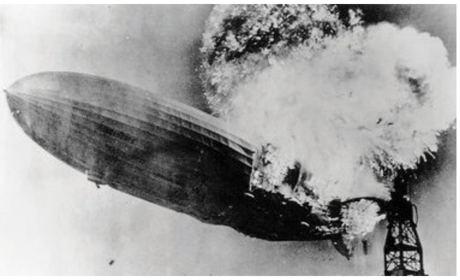


Figure $6.1.1$: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

To simplify the writing of reactions, we use formulas instead of names when we describe a reaction. We can also use symbols to represent other words in the reaction. A plus sign connects the initial substances (and final substances, if there is more than one), and an arrow ($\rightarrow$) represents the chemical change:

$$\mathrm{H_2 + O_2 \rightarrow H_2O} \tag{6.1.1}$$

This statement is one example of a **chemical equation**, an abbreviated way of using symbols to represent a chemical change. The substances on the left side of the arrow are called **reactants**, and the substances on the right side of the arrow are called **products**. It is not uncommon to include a phase label with each formula—(s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for a substance dissolved in water, also known as an *aqueous solution*. If we included phase labels for the reactants and products, under normal environmental conditions, the reaction would be as follows:

$$\mathrm{H_2(g) + O_2(g) \rightarrow H_2O(\ell)} \tag{6.1.2}$$

This equation is still not complete because *it does not satisfy the* ***law of conservation of matter***. Count the number of atoms of each element on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there are two H atoms and only one oxygen atom. The equation is not balanced because the number of oxygen atoms on each side is not the same (Figure $6.1.2$).

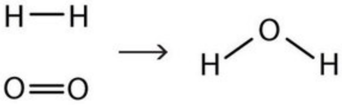


Figure $6.1.2$: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is not balanced as written.

To make this chemical equation conform to the law of conservation of matter, we must revise the amounts of the reactants and the products as necessary to get the *same* number of atoms of a given element on each side. Because every substance has a characteristic chemical formula, we cannot change the chemical formulas of the individual substances. For example, we cannot change the formula for elemental oxygen to O. However, we can assume that different numbers of reactant molecules or product molecules may be involved. For instance, perhaps two water molecules are produced, not just one:

$$\mathrm{H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)} \tag{6.1.3}$$

The **2** preceding the formula for water is called a **coefficient**. It implies that two water molecules are formed. There are now two oxygen atoms on each side of the equation.

> This point is so important that we should repeat it. You *cannot* change the formula of a chemical substance to balance a chemical reaction! You *must* use the proper chemical formula of the substance.

Unfortunately, by inserting the coefficient 2 in front of the formula for water, we have also changed the number of hydrogen atoms on the product side as well. As a result, we no longer have the same number of hydrogen atoms on each side. This can be easily fixed, however, by putting a coefficient of 2 in front of the diatomic hydrogen reactant:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell) \tag{6.1.4}$$

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The law of conservation of matter is satisfied because we now have the *same number* of atoms of each element in the reactants and in the products. We say that the reaction is now **balanced** (Figure 6.1.3). Note: The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

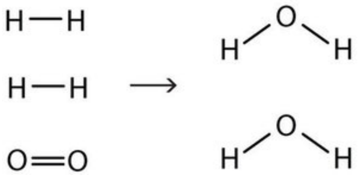


Figure 6.1.3: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is now balanced.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

mple

Is each chemical equation balanced?

a. $2Na(s) + O_2(g) \rightarrow 2Na_2O(s)$
b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
c. $AgNO_3(aq) + 2KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

Solution

a. By counting, we find two sodium atoms and two oxygen atoms in the reactants and four sodium atoms and two oxygen atoms in the products. This equation is not balanced.
b. The reactants have one carbon atom, four hydrogen atoms, and four oxygen atoms. The products have one carbon atom, four hydrogen atoms, and four oxygen atoms. This equation is balanced.
c. The reactants have one silver atom, one nitrogen atom, three oxygen atoms, two potassium atoms, and two chlorine atoms. The products have one silver atom, one chlorine atom, one potassium atom, one nitrogen atom, and three oxygen atoms. Because there are different numbers of chlorine and potassium atoms, this equation is not balanced.

rcise

Is each chemical equation balanced?

a. $2Hg_{(\ell)} + O_{2(g)} \rightarrow Hg_2O_{2(s)}$
b. $C_2H_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(\ell)}$
c. $Mg(NO_3)_{2(s)} + 2Li_{(s)} \rightarrow Mg_{(s)} + 2LiNO_{3(s)}$.

Answer a:

balanced

Answer b:

O is not balanced; the 4 atoms of oxygen on the left does not balance with the 6 oxygen atoms on the right

Answer c:

balanced

6.2: Balancing Chemical Equations

Learning Objectives

- Balance chemical equations.

How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a back-and-forth (or trial-and-error) approach is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient if necessary. Then check another element, going back and forth from one side of the equation to another, until each element has the same number of atoms on both sides of the arrow. In many cases, it does not matter which element is balanced first and which is balanced last, as long as all elements have the same number of atoms on each side of the equation.

Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product. Write the skeleton equation.
2. 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.
3. Balance each element one at a time by placing coefficients in front of the formulas. No coefficient is written for a 1. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation. NEVER change the subscripts in a chemical formula - you can only balance equations by using coefficients.
4. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
5. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

For example, to balance the equation

Step 1: Write the skeleton equation with the correct formulas.

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + HCl} \tag{6.2.1}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

$$\begin{array}{ll} \textbf{Reactants} & \textbf{Products} \\ 1\text{ C atom} & 1\text{ C atom} \\ 4\text{ H ions} & 1\text{ H ions} \\ 2\text{ Cl atom} & 5\text{ Cl atoms} \end{array} \tag{6.2.2}$$

Step 3: We find that both sides are already balanced with one carbon atom. So we proceed to balance the hydrogen atoms. We find that the reactant side has four hydrogen atoms, so the product side must also have four hydrogen atoms. This is balanced by putting a 4 in front of the HCl:

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{6.2.3}$$

$$\begin{array}{ll} \textbf{Reactants} & \textbf{Products} \\ 1\text{ C atom} & 1\text{ C atom} \\ 4\text{ H ions} & 4\text{ H ions} \\ 2\text{ Cl atom} & 8\text{ Cl atoms} \end{array} \tag{6.2.4}$$

Now each side has four hydrogen atoms. The product side has a total of eight chlorine atoms (four from the CCl_4 and four from the four molecules of HCl), so we need eight chlorine atoms as reactants. Because elemental chlorine is a diatomic molecule, we need four chlorine molecules to get a total of eight chlorine atoms. We add another 4 in front of the Cl_2 reactant:

$$\mathrm{CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{6.2.5}$$

$$\begin{array}{ll} \textbf{Reactants} & \textbf{Products} \\ 1\text{ C atom} & 1\text{ C atom} \\ 4\text{ H ions} & 4\text{ H ions} \\ 8\text{ Cl atom} & 8\text{ Cl atoms} \end{array} \tag{6.2.6}$$

Step 3: Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced. And, the coefficients are in the lowest possible ratio.

✓ Example 6.2.2

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: Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{6.2.7}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

$$\begin{array}{ll} \textbf{Reactants} & \textbf{Products} \\ 1\ \mathrm{Pb\ atom} & 1\ \mathrm{Pb\ atom} \\ 2\ \mathrm{NO_3^-}\ \text{ions} & 1\ \mathrm{NO_3^-}\ \text{ions} \\ 1\ \mathrm{Na\ atom} & 1\ \mathrm{Na\ atom} \\ 1\ \mathrm{Cl\ atom} & 2\ \mathrm{Cl\ atoms} \end{array} \tag{6.2.8}$$

Step 3: Solve. 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:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{6.2.9}$$

Step 4: The new count for each atom and polyatomic ion becomes:

$$\begin{array}{ll} \textbf{Reactants} & \textbf{Products} \\ 1\ \mathrm{Pb\ atom} & 1\ \mathrm{Pb\ atom} \\ 2\ \mathrm{NO_3^-}\ \text{ions} & 2\ \mathrm{NO_3^-}\ \text{ions} \\ 2\ \mathrm{Na\ atom} & 2\ \mathrm{Na\ atom} \\ 2\ \mathrm{Cl\ atom} & 2\ \mathrm{Cl\ atoms} \end{array} \tag{6.2.10}$$

Step 5: Think about the result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation. And, the coefficients are in the lowest possible ratio.

? Exercise 6.2.2

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose ($C_6H_{12}O_6$) are converted to ethanol (C_2H_5OH) and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.

***Commercial use of fermentation**. (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer

$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$

6.3: Avogadro's Number

Figure 6.3.1 (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 $6.3.2$: 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 $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{F_2}$, $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as $\mathrm{H_2O}$ and $\mathrm{CO_2}$ exist as molecules and so the molecule is their representative particle. For ionic compounds such as NaCl and $\mathrm{Ca(NO_3)_2}$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.

Figure 6.3.3: 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 (6.02×10^{23}) 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?

SECTION OVERVIEW

6.4: The Mole

The mole is the unit of measurement in the International System of Units (SI) for amount of substance. It is defined as the amount of a chemical substance that contains as many elementary entities (e.g., atoms, molecules, ions, electrons, or photons). This number is expressed by the Avogadro constant, which has a value of $6.022140857 \times 10^{23}\ mol^{-1}$. The mole is one of the base units of the SI, and has the unit symbol mol.

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6.5: Conversions Between Mass and Number of Particles

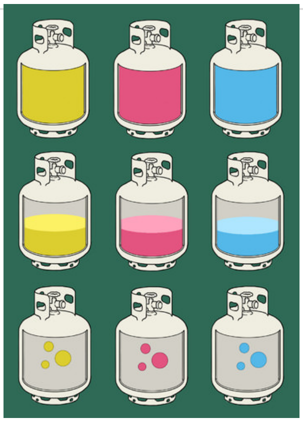

Figure 6.5.1 (Credit: Laura Guerin; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

How much gas is there?

Avogadro was interested in studying gases. He theorized that equal volumes of gases under the same conditions contained the same number of particles. Other researchers studied how many gas particles were in specific volumes of gases. Eventually, scientists were able to develop the relationship between number of particles and mass, using the idea of moles.

Conversions Between Mass and Number of Particles

In "Conversions Between Moles and Mass", you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and the mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to grams. In order to convert from mass to number of particles or vice-versa, a conversion to moles is required.

Figure 6.5.2: Conversion from number of particles to mass, or from mass to number of particles requires two steps. (Credit: Christopher Auyeung; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Example 6.5.1: Converting Mass to Particles

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

Solution

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

Known

- Molar mass $\mathrm{Cl_2} = 70.90\ \mathrm{g/mol}$
- $20.0\ \mathrm{g\ Cl_2}$

Unknown

- number of molecules of $\mathrm{Cl_2}$

Use two conversion factors. The first converts grams of $\mathrm{Cl_2}$ to moles. The second converts moles of $\mathrm{Cl_2}$ to the number of molecules.

Step 2: Calculate.

$$20.0\ \mathrm{g\ Cl_2} \times \frac{1\ \mathrm{mol\ Cl_2}}{70.90\ \mathrm{g\ Cl_2}} \times \frac{6.02 \times 10^{23}\ \mathrm{molecules\ Cl_2}}{1\ \mathrm{mol\ Cl_2}} = 1.70 \times 10^{23}\ \mathrm{molecules\ Cl_2}$$

The problem is done using two consecutive conversion factors. There is no need to explicitly calculate the moles of $\mathrm{Cl_2}$.

Step 3: Think about your result.

Since the given mass is less than half of the molar mass of chlorine, the resulting number of molecules is less than half of Avogadro's number.

Summary

- Calculations are illustrated for conversions between mass and number of particles.

Review

1. Why can’t we convert directly from number of particles to grams?
2. How many atoms of chlorine are present in 1.70×10^{23} molecules Cl_2?
3. How many molecules of BH_3 are in 14.32 grams BH_3?

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6.6: Molar Mass

Figure 6.6.1 (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 g, the molar mass of zinc is 65.38 g and the molar mass of gold is 196.97 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 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 g while one mole of sodium sulfide formula units has a mass of 78.04 g The molar masses are $44.01 \text{ g/mol}$and 78.04 g/molrespectively. 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 6.6.1: 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.

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

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

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

$$\text{Molar mass of } \mathrm{Ca(NO_3)_2} = 40.08 \text{ g} + 28.02 \text{ g} + 96.00 \text{ g} = 164.10 \text{ g/mol}$$

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 $CaCl_2$.

6.7: Conversions Between Moles and Mass

Figure 6.7.1 (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 $\left(\mathrm{CaCl_2}\right)$. 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 $110.98 \text{ g}/\text{mol}$ The conversion factor that can be used is then based on the equality that $1 \text{ mol} = 110.98 \text{ g } \mathrm{CaCl_2}$. Dimensional analysis will allow you to calculate the mass of $\mathrm{CaCl_2}$ that you should measure.

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

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

Figure 6.7.2: 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 6.7.1: 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 $\mathrm{Cr} = 52.00 \text{ g}/\text{mol}$
- 0.560 mol Cr

Unknown

- 0.560 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 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 6.7.2: Converting Mass to Moles

A certain reaction produces 2.81 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 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?

6.8: Conversions Between Moles and Atoms

Figure 6.8.1 (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 6.8.1: 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 $= 4.72 \times 10^{24}$
- $1 \text{ mole} = 6.02 \times 10^{23}$ atoms

Unknown

- $4.72 \text{ x } 10^{24}$ = ? 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.

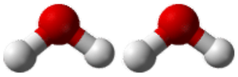


Figure 6.8.2: Two water molecules contain 4 hydrogen atoms and 2 oxygen atoms. A mole of water molecules contains 2 moles of hydrogen atoms and 1 mole of oxygen atoms. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Water-3D-balls-A.png(opens in new window); License: Public Domain)

Example 6.8.2: 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

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

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?

6.9: 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 6.9.1):

$$\mathrm{Zn(s)} + 2\,\mathrm{HCl(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{ZnCl_2(aq)} \tag{6.9.1}$$

This is one example of what is sometimes called a *single replacement reaction* because Zn replaces H in combination with Cl.

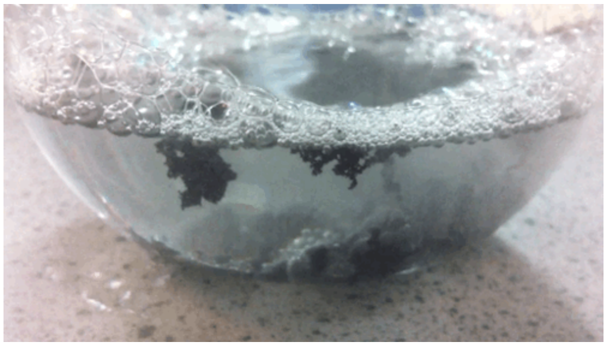


Figure 6.9.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 6.9.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn(s)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{Cl^-(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Cl^-(aq)}$$

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,

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

zinc atoms are oxidized to $\mathrm{Zn^{2+}}$. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn} \rightarrow \mathrm{Zn^{2+}} + 2\,\mathrm{e^-}$$

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:

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

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.

$$\begin{array}{r} Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ \underline{2H^+ + \cancel{2e^-} \rightarrow H_2} \\ Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{array}$$

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 $6.9.1$: 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:

$$Ag^+ + Al \rightarrow Ag + Al^{3\,+}$$

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:

$$Ag^+ + e^- \rightarrow Ag$$

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

Oxidation half-reaction:

$$Al \rightarrow Al^{3\,+} + 3\,e^-$$

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

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

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 6.9.1

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:

$$\mathrm{Cd(s) + 2\,NiOOH(s) + 2\,H_2O(\ell) \rightarrow Cd(OH)_2(s) + 2\,Ni(OH)2\ (s)}$$

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:

$$\mathrm{2\,Li(s) + I_2(s) \rightarrow 2\,LiI(s)}$$

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.

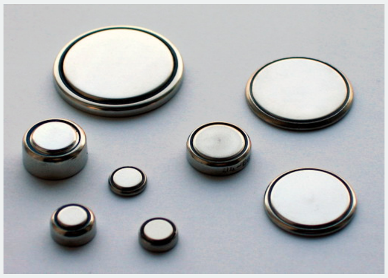


Figure 6.9.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

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 ($\mathrm{CH_3CHO}$) molecule takes on an oxygen atom to become acetic acid ($\mathrm{CH_3COOH}$).

$$\mathrm{2\,CH_3CHO + O_2 \rightarrow 2\,CH_3COOH}$$

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:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$

Table 6.9.1: Oxidation-Reduction Reactions and the Changes in Oxygen and Hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

✓ Example 6.9.2

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 6.9.2

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.

6.10: Recognizing Redox Reactions

Learning Objectives

- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.
3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number (except when it exists as the hydride ion [H^-], in which case rule 2 prevails).
4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

Here are some examples for practice. In H_2, both H atoms have an oxidation number of 0 by rule 1. In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1 by rule 2. In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1. We can use rule 4 to determine oxidation numbers for the atoms in SO_2. Each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 6.10.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $Ca(NO_3)_2$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
3. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation $x + 3(-2) = -1$

   where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

   $x + (-6) = -1 x = +5$

   Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 6.10.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer

H: +1; O: −2; P: +5

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

Example 6.10.2:

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

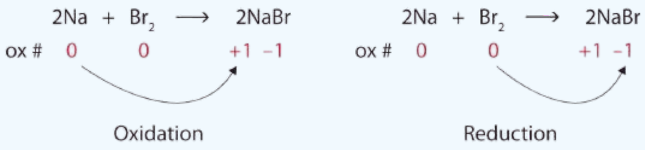
$$2\,\mathrm{Na} + \mathrm{Br_2} \rightarrow 2\,\mathrm{NaBr}$$

Solution

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

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

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 6.10.2

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

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$$

Answer

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

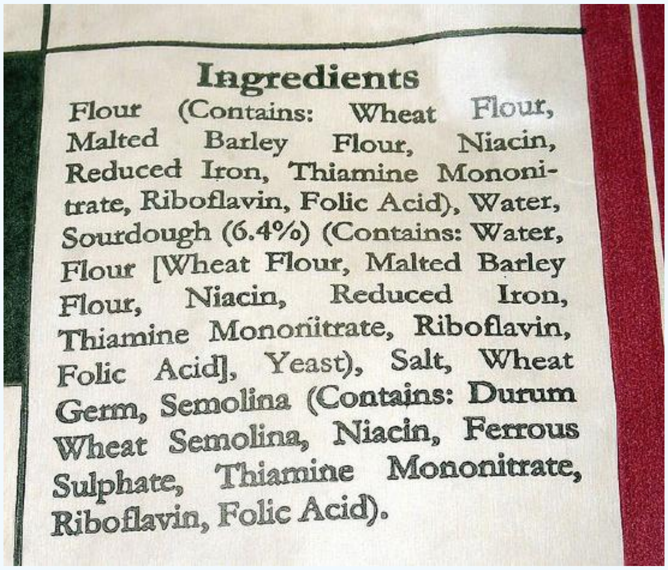
Oxidation reactions can become quite complex, as attested by the following redox reaction:

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

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced?

Food and Drink Application: Fortifying Food with Iron

Iron is an essential mineral in our diet; iron-containing compounds like the heme protein in hemoglobin could not function without it. Most biological iron has the form of the Fe^{2+} ion; iron with other oxidation numbers is almost inconsequential in human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+}, so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+} compounds are the most logical substances to use, some foods use "reduced iron" as an ingredient (bread and breakfast cereals are the most well-known examples). Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?



Ingredients

Flour (Contains: Wheat Flour, Malted Barley Flour, Niacin, Reduced Iron, Thiamine Mononitrate, Riboflavin, Folic Acid), Water, Sourdough (6.4%) (Contains: Water, Flour [Wheat Flour, Malted Barley Flour, Niacin, Reduced Iron, Thiamine Mononitrate, Riboflavin, Folic Acid], Yeast), Salt, Wheat Germ, Semolina (Contains: Durum Wheat Semolina, Niacin, Ferrous Sulphate, Thiamine Mononitrate, Riboflavin, Folic Acid).

Figure 6.10.1 Ingredients. Many prepared foods list reduced iron in their ingredients list.

The ingredients list contains Flour (Contains: wheat flour, malted barley flour, niacin, reduced iron, thiamine mononitrate, riboflavin, folic acid), water, sourdough (6.4%) (contains: water, flour [wheat flour, malted barley flour, niacin, reduced iron, thiamine mononitrate, riboflavin, folic acid], yeast), salt, wheat germ, semolina (contains: durum wheat semolina, niacin, ferrous sulphate, thiamine mononitrate, riboflavin, folic acid).

Although it is difficult to establish conclusive reasons, a search of scientific and medical literature suggests a few reasons. One reason is that fine iron filings do not affect the taste of the product. The size of the iron powder (several dozen micrometers) is not noticeable when chewing iron-supplemented foods, and the tongue does not detect any changes in flavor that can be detected when using Fe^{2+} salts. Fe^{2+} compounds can affect other properties of foodstuffs during preparation and cooking, like dough pliability, yeast growth, and color. Finally, of the common iron substances that might be used, metallic iron is the least expensive. These factors appear to be among the reasons why metallic iron is the supplement of choice in some foods.

Key Takeaways

- Oxidation numbers are used to keep track of electrons in atoms.
- There are rules for assigning oxidation numbers to atoms.
- Oxidation is an increase in oxidation number (loss of electrons); reduction is a decrease in oxidation number (gain of electrons).

CHAPTER OVERVIEW

7: Reactions in Solution

7.1: SOLUTIONS - HOMOGENEOUS MIXTURES

LEARNING OBJECTIVES

- Learn terminology involving solutions.
- Explain the significance of the statement "like dissolves like."
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. By major and minor we mean whichever component has the greater or lesser presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. However, here we will confine the discussion to solutions for which the major component and the minor component are obvious.

Figure 7.1.1: Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water, while air is a solution of a gaseous solute ($\mathrm{O_2}$) in a gaseous solvent ($\mathrm{N_2}$). In all cases, however, the overall phase of the solution is the same phase as the solvent. Table 7.1.1 lists some common types of solutions, with examples of each.

Table 7.1.1: Types of Solutions

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

✓ EXAMPLE 7.1.1: SUGAR AND WATER

A solution is made by dissolving 1.00 g of sucrose ($\mathrm{C_{12}H_{22}O_{11}}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

? EXERCISE 7.1.1

A solution is made by dissolving 3.33 g of $\mathrm{HCl(g)}$ in 40.0 g of liquid methyl alcohol ($\mathrm{CH_3OH}$). Identify the solvent and solute in the resulting solution.

Answer

solute: $\mathrm{HCl(g)}$

solvent: $\mathrm{CH_3OH}$

LIKE DISSOLVES LIKE

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water—it is this oxygen that the fish take in through their gills. The reason we can enjoy carbonated sodas is also due to a nonpolar compound that dissolves in water. Pepsi-cola and all the other sodas have carbon dioxide gas, CO_2, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

Table 7.1.2: Summary of Solubilities

Solute (Polarity of Compound)	Solvent (Polarity of Compound)	Dominant Intermolecular Force	Is Solution Formed?
Polar	Polar	Dipole-Dipole Force and/or Hydrogen Bond	yes
Non-polar	Non-polar	Dispersion Force	yes
Polar	Non-polar		no
Non-polar	Polar		no
Ionic	Polar	Ion-Dipole	yes
Ionic	Non-polar		no

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges, a solution does not form. When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in Chapter 10). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water.

Figure 7.1.2: Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

✓ EXAMPLE 7.1.2: POLAR AND NONPOLAR SOLVENTS

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

? EXERCISE 7.1.2

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

Answer

H_2O, because both experience hydrogen bonding.

✓ EXAMPLE 7.1.3

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol (CH_3OH)
b. sodium sulfate (\ce{Na2SO4}\))
c. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

a. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
b. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
c. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? EXERCISE 7.1.3: TOLUENE

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

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

SUMMARY

- Solutions are composed of a solvent (major component) and a solute (minor component).
- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

7.2: Solutions of Solids Dissolved in Water- How to Make Rock Candy

Learning Objectives

- Define electrolytes and non electrolytes
- Explain why solutions form.
- Discuss the idea of water as the "universal solvent".
- Explain how water molecules attract ionic solids when they dissolve in water.

We have learned that solutions can be formed in a variety of combinations using solids, liquids, and gases. We also know that solutions have constant composition, and that this composition can be varied up to a point to maintain the homogeneous nature of the solution. But how exactly do solutions form? Why is it that oil and water will not form a solution, and yet vinegar and water will? Why could we dissolve table salt in water, but not in vegetable oil? The reasons why solutions will form will be explored in this section, along with a discussion of why water is used most frequently to dissolve substances of various types.

Solubility and Saturation

Table salt (NaCl) readily dissolves in water. In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is specified as the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table $7.2.1$ lists the solubilities of some simple ionic compounds. These solubilities vary widely. NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table $7.2.1$: Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated, but rather concentrated. In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.The figure below illustrates the above process and shows the distinction between unsaturated and saturated.

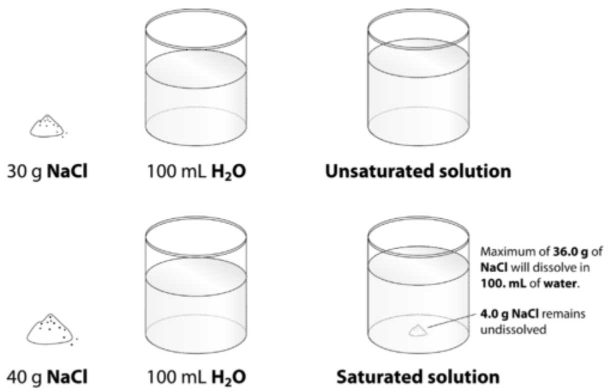


Figure 7.2.1: When 30.0 g of NaCl is added to 100 mL, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution.

How can you tell if a solution is saturated or unsaturated? If more solute is added and it does not dissolve, then the original solution was saturated. If the added solute dissolves, then the original solution was unsaturated. A solution that has been allowed to reach equilibrium, but which has extra undissolved solute at the bottom of the container, must be saturated.

Electrolyte Solutions: Dissolved Ionic Solids

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

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 7.2.1).

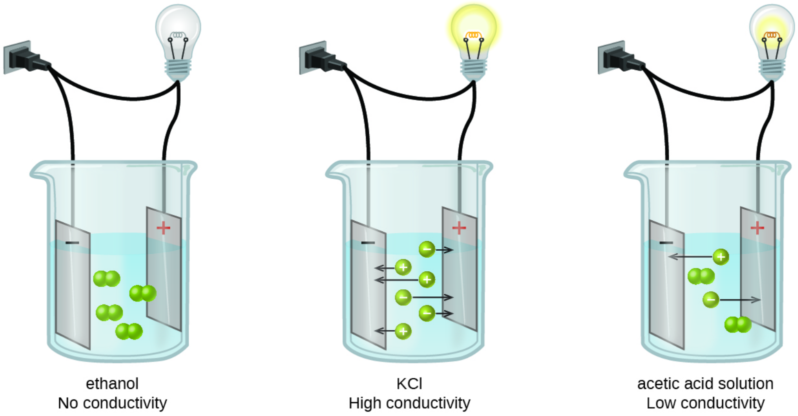


Figure 7.2.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram shows three separate beakers. Each has a wire plugged into a wall outlet. In each case, the wire leads from the wall to the beaker and is split resulting in two ends. One end leads to a light bulb and continues on to a rectangle labeled with a plus sign. The other end leads to a rectangle labeled with a minus sign. The rectangles are in a solution. In the first beaker, labeled “Ethanol No Conductivity,” four pairs of linked small green spheres suspended in the solution between the rectangles. In the second beaker, labeled “K C l Strong Conductivity,” six individual green spheres, three labeled plus and three labeled minus are suspended in the solution. Each of the six spheres has an arrow extending from it pointing to the rectangle labeled with the opposite sign. In the third beaker, labeled “Acetic acid solution Weak conductivity,” two pairs of joined green spheres and two individual spheres, one labeled plus and one labeled minus are shown suspended between the two rectangles. The plus labeled sphere has an arrow pointing to the rectangle labeled minus and the minus labeled sphere has an arrow pointing to the rectangle labeled plus.

Water and other polar molecules are attracted to ions, as shown in Figure 7.2.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

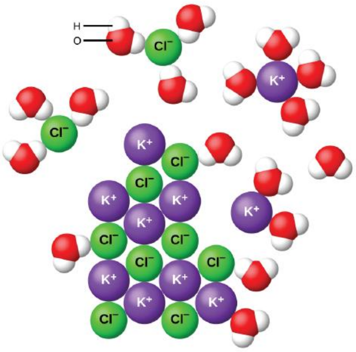


Figure 7.2.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight green spheres labeled C l superscript minus mixed and touching near the center of the diagram. Outside of this cluster of spheres are seventeen clusters of three spheres, which include one red and two white spheres. A red sphere in one of these clusters is labeled O. A white sphere is labeled H. Two of the green C l superscript minus spheres are surrounded by three of the red and white clusters, with the red spheres closer to the green spheres than the white spheres. One of the K superscript plus purple spheres is surrounded by four of the red and white clusters. The white spheres of these clusters are closest to the purple spheres.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

✓ Example 7.2.1: Identifying Ionic Compounds

Which compound(s) will dissolve in solution to separate into ions?

a. LiF

b. P_2F_5
c. C_2H_5OH

Solution

LiF will separate into ions when dissolved in solution, because it is an ionic compound. P_2F_5 and C_2H_5OH are both covalent and will stay as molecules in a solution.

? Exercise 7.2.1

Which compounds will dissolve in solution to separate into ions?

a. $C_6H_{12}O_{11}$, glucose
b. CCl_4
c. $CaCl_2$
d. $AgNO_3$

Answer

c & d

How Temperature Influences Solubility

The **solubility** of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature. Solubility is often measured as the grams of solute per 100 g of solvent. The solubility of sodium chloride in water is 36.0 g per 100 g water at 20°C. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubility is specific for a particular solvent. We will consider solubility of material in water as solvent.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (Figure $7.2.4$).

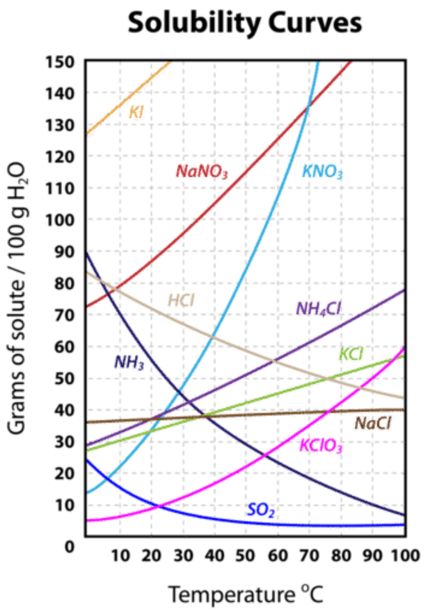


Figure $7.2.4$: Solubility curves for several compounds.

Notice how the temperature dependence of $NaCl$ is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of $NaCl$. The curve for KNO_3, on the other hand, is very steep and so an increase in temperature dramatically increases the solubility of KNO_3.

Several substances—HCl, $\mathrm{NH_3}$, and $\mathrm{SO_2}$—have solubility that decreases as temperature increases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increase. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that 80 g of $\mathrm{KNO_3}$ is added to $100\ \mathrm{g}$ of water at $30^\mathrm{o}\mathrm{C}$. According to the solubility curve, approximately 48 g of $\mathrm{KNO_3}$ will dissolve at $30^\mathrm{o}\mathrm{C}$. This means that the solution will be saturated since 48 g is less than 80 g. We can also determine that there will be $80 - 48 = 32\ \mathrm{g}$ of undissolved $\mathrm{KNO_3}$ remaining at the bottom of the container. Now suppose that this saturated solution is heated to $60^\mathrm{o}\mathrm{C}$. According to the curve, the solubility of $\mathrm{KNO_3}$ at $60^\mathrm{o}\mathrm{C}$ is about $107\ \mathrm{g}$. Now the solution is unsaturated since it contains only the original 80 g of dissolved solute. Now suppose the solution is cooled all the way down to $0^\mathrm{o}\mathrm{C}$. The solubility at $0^\mathrm{o}\mathrm{C}$ is about 14 g, meaning that $80 - 14 = 66$ g of the $\mathrm{KNO_3}$ will re-crystallize.

Summary

- Solubility is the specific amount of solute that can dissolve in a given amount of solvent.
- Saturated and unsaturated solutions are defined.
- Ionic compounds dissolve in polar solvents, especially water. This occurs when the positive cation from the ionic solid is attracted to the negative end of the water molecule (oxygen) and the negative anion of the ionic solid is attracted to the positive end of the water molecule (hydrogen).
- Water is considered the universal solvent since it can dissolve both ionic and polar solutes, as well as some nonpolar solutes (in very limited amounts).
- The solubility of a solid in water increases with an increase in temperature.

Vocabulary

- **Miscible** - Liquids that have the ability to dissolve in each other.
- **Immiscible** - Liquids that do not have the ability to dissolve in each other.
- **Electrostatic attraction** - The attraction of oppositely charged particles.

7.2: Solutions of Solids Dissolved in Water- How to Make Rock Candy is shared under a CK-12 license and was authored, remixed, and/or curated by Marisa Alviar-Agnew & Henry Agnew.

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7.3: Specifying Solution Concentration- Molarity

Learning Objectives

- Use molarity to determine quantities in chemical reactions.
- Use molarity as a conversion factor in calculations.

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Of all the quantitative measures of concentration, molarity is the one used most frequently by chemists. **Molarity** is defined as the number of moles of solute per liter of solution.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{7.3.1}$$

The symbol for molarity is M or moles/liter. Chemists also use square brackets to indicate a reference to the molarity of a substance. For example, the expression $\left[\mathrm{Ag}^{+}\right]$ refers to the molarity of the silver ion in solution. Solution concentrations expressed in molarity are the easiest to perform calculations with, but the most difficult to make in the lab. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl (aq).” This is read as "a 3.00 ***molar*** sodium chloride solution," meaning that there are 3.00 moles of NaOH dissolved per one liter of solution.

> *Be sure to note that molarity is calculated as the total volume of the* ***entire*** *solution, not just volume of solvent! The solute contributes to total volume.*

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?

Step 1: First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\ g\cancel{HCl} \times \frac{1\ mol\ HCl}{36.5\ g\cancel{HCl}} = 0.614\, mol\ HCl$$

Step 2: Now we can use the definition of molarity to determine a concentration:

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

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

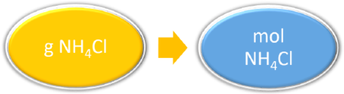
Example 7.3.1

A solution is prepared by dissolving 42.23 g of $\mathrm{NH_4Cl}$ into enough water to make 500.0 mL of solution. Calculate its molarity.

Solution

Solutions to Example 13.6.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Mass $= 42.23 \text{ g NH}_4\text{Cl}$ Volume solution $= 500.0 \text{ mL} = 0.5000 \text{ L}$ Find: Molarity = ? M
List other known quantities.	Molar mass $\mathrm{NH_4Cl} = 53.50 \text{ g/mol}$

Steps for Problem Solving	
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles.  $\frac{1\ mol\ NH_4Cl}{53.50 g\ NH_4Cl}$ 2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters. $M = \frac{mol\ NH_4Cl}{L\ solution}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $42.23\ \cancel{g\ NH_4Cl} \times \frac{1\ mol\ NH_4Cl}{53.50\ \cancel{g\ NH_4Cl}} = 0.7893\ mol\ NH_4Cl$ $\frac{0.7893\ mol\ NH_4Cl}{0.5000\ L\ solution} = 1.579\ M$
Think about your result.	The molarity is $1.579\ M$, meaning that a liter of the solution would contain $1.579\ mol\ NH_4Cl$. Four significant figures are appropriate.

? Exercise $7.3.1A$

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M $C_6H_{12}O_6$

? Exercise $7.3.1B$

What is the concentration, in mol/L, where $137\ g$ of $NaCl$ has been dissolved in enough water to make $500\ mL$ of solution?

Answer

4.69 M NaCl

Using Molarity in Calculations

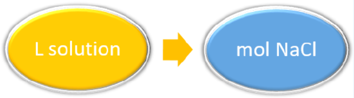
Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition.

✓ Example 7.3.2: Determining Moles of Solute, Given the Concentration and Volume of a Solution

For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

Solution



$$\frac{.887\ mol\ NaCl}{1\ L\ solution}$$

$$0.108\ L\ \cancel{solution} \times \frac{0.887\ mol\ NaCl}{1 L\ \cancel{solution}} = 0.0958\ mol\ NaCl$$

If we used the definition approach, we get the same answer, but now we are using conversion factor skills.

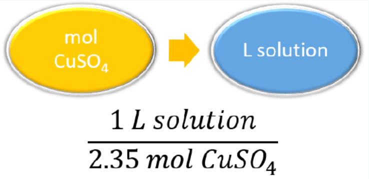
Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

✓ Example 7.3.3: Determining Volume of a Solution, Given the Concentration and Moles of Solute

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:



$$4.88\ mol\ \cancel{CuSO_4} \times \frac{1\ L\ solution}{2.35\ mol\ \cancel{CuSO_4}} = 2.08\ L\ of\ solution$$

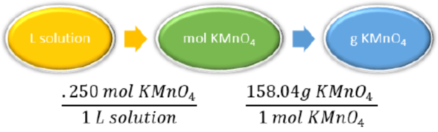
In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams. The following example illustrates this.

✓ Example 7.3.4

A chemist needs to prepare $3.00\ \mathrm{L}$ of a $0.250\ \mathrm{M}$ solution of potassium permanganate $\left(\mathrm{KMnO_4}\right)$. What mass of $\mathrm{KMnO_4}$ does she need to make the solution?

Solution

Solutions to Example 13.6.4

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Molarity $= 0.250\ \mathrm{M}$ Volume $= 3.00\ \mathrm{L}$ Find: Mass $\mathrm{KMnO_4}$ $= ?\ \mathrm{g}$
List other known quantities.	Molar mass $\mathrm{KMnO_4} = 158.04\ \mathrm{g/mol}$ 0.250 mol $KMnO_4$ to 1 L of $KMnO_4$ solution
Plan the problem.	
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $\mathrm{mol\ KMnO_4} = 0.250\ \mathrm{M\ KMnO_4} \times 3.00\ \mathrm{L} = 0.750\ \mathrm{mol}$ $3.00\ \cancel{L\ solution} \times \frac{0.250\ \mathrm{mol}\ \cancel{\mathrm{KMnO_4}}}{1\ \cancel{L\ solution}} \times \frac{158.04\ \mathrm{g\ KMnO_4}}{1\ \mathrm{mol}\ \cancel{\mathrm{KMnO_4}}} = 119\ \mathrm{g\ KM}$
Think about your result.	When 119 g of potassium permanganate is dissolved into water to make $3.00\ \mathrm{L}$ of solution, the molarity is $0.250\ \mathrm{M}$.

? Exercise $7.3.4A$

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer

1.74 L

Exercise $7.3.4B$

Answer the problems below using concentration as a conversion factor.

a. What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?
b. What volume of 1.50 M HCl solution contains 10.0 g of hydrogen chloride?

Answer a

6.12 g

Answer b

183 mL or 0.183L

How to Indicate Concentration

- Square brackets are often used to represent concentration, e.g., [NaOH] = 0.50 M.
- Use the capital letter M for molarity, not a lower case m (this is a different concentration unit called *molality*).

Watch as the Flinn Scientific Tech Staff demonstrates "How To Prepare Solutions."

It is important to note that there are many different ways you can set up and solve your chemistry equations. Some students prefer to answer multi-step calculations in one long step, while others prefer to work out each step individually. Neither method is necessarily better or worse than the other method—whichever makes the most sense to ***you*** is the one that you should use. In this text, we will typically use unit analysis (also called dimension analysis or factor analysis).

Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

7.4: SOLUTION DILUTION

LEARNING OBJECTIVES

- Explain how concentrations can be changed in the lab.
- Understand how stock solutions are used in the laboratory.

We are often concerned with how much solute is dissolved in a given amount of solution. We will begin our discussion of solution concentration with two related and relative terms: **dilute** and **concentrated**.

- A **dilute** solution is one in which there is a relatively small amount of solute dissolved in the solution.
- A **concentrated** solution contains a relatively large amount of solute.

These two terms do not provide any quantitative information (actual numbers), but they are often useful in comparing solutions in a more general sense. These terms also do not tell us whether or not the solution is saturated or unsaturated, or whether the solution is "strong" or "weak". These last two terms will have special meanings when we discuss acids and bases, so be careful not to confuse them.

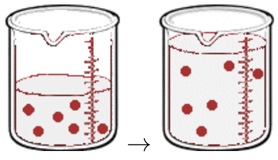
STOCK SOLUTIONS

It is often necessary to have a solution with a concentration that is very precisely known. Solutions containing a precise mass of solute in a precise volume of solution are called **stock (or standard) solutions.** To prepare a standard solution, a piece of lab equipment called a volumetric flask should be used. These flasks range in size from 10 mL to 2000 mL and are carefully calibrated to a single volume. On the narrow stem is a **calibration mark**. The precise mass of solute is dissolved in a bit of the solvent, and this is added to the flask. Then, enough solvent is added to the flask until the level reaches the calibration mark.

Often, it is convenient to prepare a series of solutions of known concentrations by first preparing a single **stock solution**, as described in the previous section. **Aliquots** (carefully measured volumes) of the stock solution can then be diluted to any desired volume. In other cases, it may be inconvenient to weigh a small mass of sample accurately enough to prepare a small volume of a dilute solution. Each of these situations requires that a solution be diluted to obtain the desired concentration.

DILUTIONS OF STOCK (OR STANDARD) SOLUTIONS

Imagine we have a salt water solution with a certain concentration. That means we have a certain amount of salt (a certain mass or a certain number of moles) dissolved in a certain volume of solution. Next, we will dilute this solution. This is done by adding more water, not more salt:



Before Dilution and After Dilution

The molarity of solution 1 is

$$M_1 = \frac{\text{moles}_1}{\text{liter}_1}$$

and the molarity of solution 2 is

$$M_2 = \frac{\text{moles}_2}{\text{liter}_2}$$

rearrange the equations to find moles:

$$\text{moles}_1 = M_1 \text{liter}_1$$

and

$$\text{moles}_2 = M_2 \text{liter}_2$$

What stayed the same and what changed between the two solutions? By adding more water, we changed the volume of the solution. Doing so also changed its concentration. **However, the number of moles of solute did not change.** So,

$$moles_1 = moles_2$$

Therefore

$$\boxed{M_1V_1 = M_2V_2} \tag{7.4.1}$$

where

- M_1 and M_2 are the concentrations of the original and diluted solutions
- V_1 and V_2 are the volumes of the two solutions

Preparing dilutions is a common activity in the chemistry lab and elsewhere. Once you understand the above relationship, the calculations are simple.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

Another common dilution problem involves calculating what amount of a highly concentrated solution is required to make a desired quantity of solution of lesser concentration. The highly concentrated solution is typically referred to as the stock solution.

✓ EXAMPLE 7.4.1: DILUTING NITRIC ACID

Nitric acid $\left(\text{HNO}_3\right)$ is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is $16\ \text{M}$. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

Solution

Solutions to Example13.7.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: M_1, Stock $\text{HNO}_3 = 16\ \text{M}$ $V_2 = 8.00\ \text{L}$ $M_2 = 0.50\ \text{M}$ Find: Volume stock $\text{HNO}_3\ (V_1) = ?\ \text{L}$
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_1. $$V_1 = \frac{M_2 \times V_2}{M_1}$$
Calculate and cancel units.	Now substitute the known quantities into the equation and solve. $$V_1 = \frac{0.50\ \text{M} \times 8.00\ \text{L}}{16\ \text{M}} = 0.25\ \text{L} \tag{7.4.2}$$
Think about your result.	$0.25\ \text{L}\ (250\ \text{mL})$ of the stock HNO_3 needs to be diluted with water to a final volume of $8.00\ \text{L}$. The dilution is by a factor of 32 to go from $16\ \text{M}$ to $0.5\ \text{M}$.

? EXERCISE 7.4.1

A 0.885 M solution of KBr with an initial volume of 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

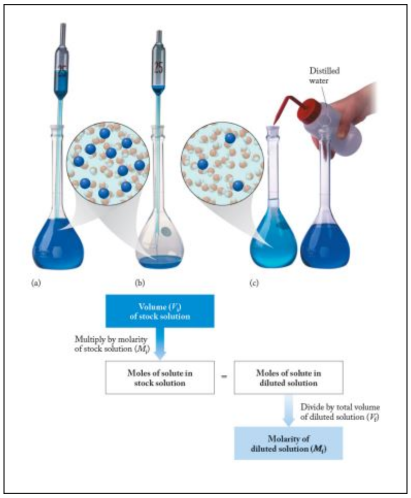
135.4 mL

> *Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).*

DILUTING AND MIXING SOLUTIONS

Diluting and Mixing Solutions

How to Dilute a Solution by CarolinaBiological



7.5: Precipitation Reactions and Solubility Guidelines

Learning Objectives

- Use solubility rules to predict whether a precipitate will form.
- Write and balance chemical equations for precipitation reactions.

There are many types of chemical reactions that you will learn about in chemistry. In this chapter, we will focus on some reactions of ionic compounds: *precipitation reactions* (a type of *double-replacement reaction*), *acid-base neutralization reactions*, and *oxidation-reduction reactions*.

The practice of barter (trading one thing for another) has been in existence since the beginning of time. In the past, for example, items like chickens were bartered for newspapers. Person A had something that person B wanted, and vice versa. So, when person A and person B traded items, they each had something new. Some chemical reactions are like that—compounds swap parts, and the products are new materials.

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:

$$\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AD} + \mathrm{CB} \tag{7.5.1}$$

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:

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s) \tag{7.5.2}$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (see Figure $7.5.1$ below). The other product of the reaction, potassium nitrate, remains soluble.

Figure $7.5.1$: Formation of lead iodide precipitate. (CC BY-NC; CK-12)

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table $7.5.1$ lists some general solubility rules. We need to consider each ionic compound (both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (*aq*) label with it, indicating that it dissolves. If a compound is not soluble, we use the (*s*) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table $7.5.1$: Solubility Rules: Soluble Compounds and Their Exceptions

These compounds generally dissolve in water (are soluble):	Exceptions:
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and $\mathrm{NH4}^+$	None
All compounds of $\mathrm{NO3}^-$ and $\mathrm{C2H3O2}^-$	None

Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table 7.5.2: Solubility Rules: Insoluble Compounds and Their Exceptions

These compounds generally do not dissolve in water (are insoluble):	Exceptions:
Compounds of CO_3^{2-} and PO_4^{3-}	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+
Compounds of OH^-	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$\mathrm{Na_2SO_4(aq) + SrCl_2(aq) \rightarrow 2\,NaCl(aq) + SrSO_4(s)}$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 7.5.2).

Figure 7.5.2: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, Wikimedia(opens in new window) [commons.wikimedia.org].

A blue solution is shown in a glass beaker. White precipitate can be seen forming at the bottom of the beaker.

✓ Example 7.5.4:

Will a precipitation reaction occur? If so, identify the products.

1. $Ca(NO_3)_2$ + KBr → ?
2. NaOH + $FeCl_2$ → ?

Solution

1. According to the solubility rules, both $Ca(NO_3)_2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr_2$ and KNO_3. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.

2. According to the solubility rules, both NaOH and $FeCl_2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)_2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)_2$ is not. Therefore, a reaction would occur, and $Fe(OH)_2(s)$ would precipitate out of solution. The balanced chemical equation is

$$2\,\mathrm{NaOH(aq)} + \mathrm{FeCl_2(aq)} \rightarrow 2\,\mathrm{NaCl(aq)} + \mathrm{Fe(OH)_2(s)}$$

Exercise 7.5.4

$$\mathrm{Sr(NO_3)_2} + \mathrm{KCl} \rightarrow$$

Answer

No reaction; all possible products are soluble.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- The periodic table or an activity series can help predict whether single-replacement reactions occur.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.
- A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.
- Solubility rules are used to predict whether some double-replacement reactions will occur.

- **4.3: Types of Chemical Reactions - Single and Double Replacement Reactions** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/beginning-chemistry.
- **11.9: Double Replacement Reactions** by CK-12 Foundation is licensed CK-12. Original source: https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/.

CHAPTER OVERVIEW

8: Acids and Bases

8.1: 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.

$$\mathrm{HCl(aq)\rightarrow H^+(aq)+Cl^-(aq)} \tag{8.1.1}$$

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:

$$\mathrm{HCl(aq)+H_2O(\ell)\rightarrow H_3O^+(aq)+Cl^-(aq)} \tag{8.1.2}$$

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:

$$\mathrm{NaOH(aq)\rightarrow Na^+(aq)+OH^-(aq)} \tag{8.1.3}$$

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

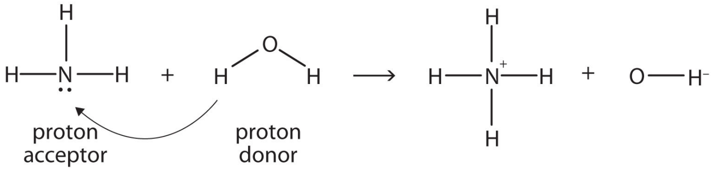
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species 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:

$$\mathrm{NH_3(aq)+H_2O(\ell)\rightleftharpoons NH_4^+(aq)+OH^-(aq)} \tag{8.1.4}$$

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:



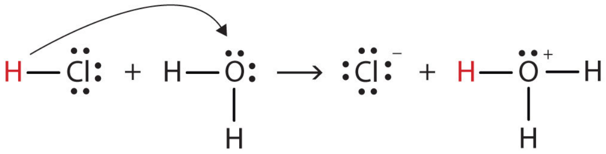
Because the water molecule *donates* a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which *accepts* the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

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:

$$\mathrm{HCl(g)+H_2O(\ell)\rightarrow H_3O^+(aq)Cl^-(aq)+H_3O^+(aq)} \tag{8.1.5}$$

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 8.1.1

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:

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

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise 8.1.1

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

$$\mathrm{H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+} \tag{8.1.6}$$

Answer

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

Exercise 8.1.2

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 HCl, $\mathrm{H_3PO_4}$, $\mathrm{NH_4^+}$ and $\mathrm{CH_3NH_3^+}$ because they are Bronsted-Lowry acids. They all give away protons. In the case of $\mathrm{HPO_4^{2-}}$, consider the following equation:

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

Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

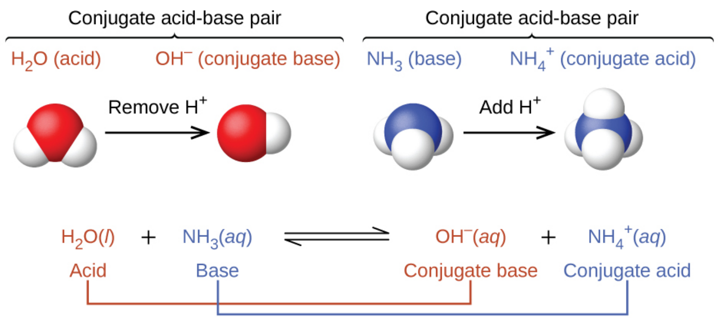
$$\mathrm{HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)}$$

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, $\mathrm{OH^-}$, and the conjugate acid of ammonia, $\mathrm{NH_4^+}$:



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

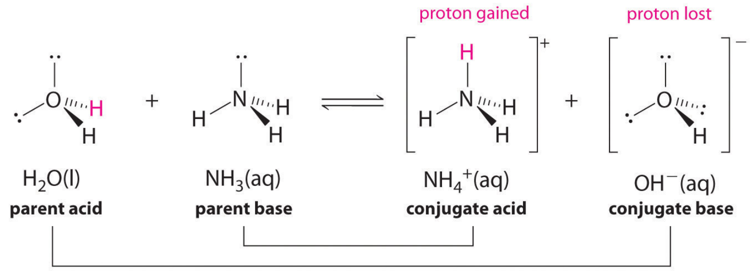


Figure 8.1.1. The pairing of parent acids and bases with conjugate acids and bases.

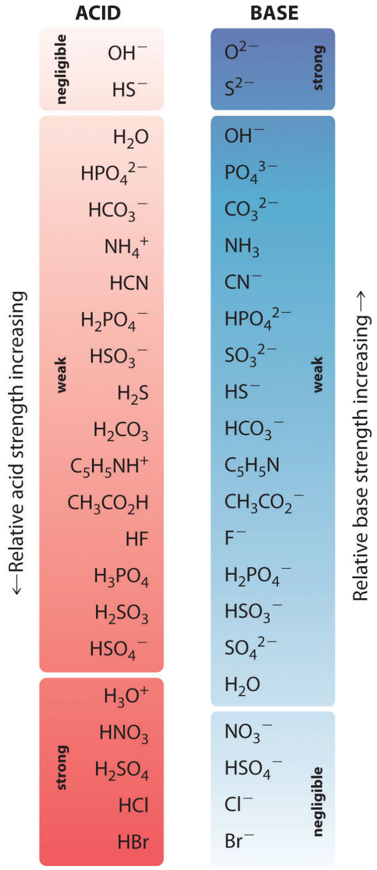


Figure 8.1.2: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

✓ Example 8.1.2

Identify the conjugate acid-base pairs in this equilibrium.

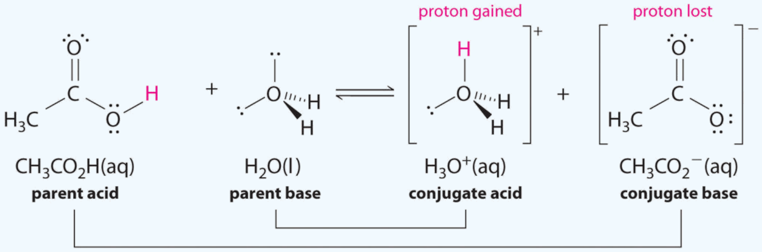
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 8.1.3

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 (CH3)3N and $(CH3)3NH^+$, where $(CH3)3NH^+$ is the conjugate acid (it has an additional proton) and (CH3)3N is the conjugate base.

Exercise 8.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$\mathrm{NH_2^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_3} + \mathrm{OH^-}$$

Answer

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

Contributions & Attributions

This page was constructed from content via the following contributor(s) and edited (topically or extensively) by the LibreTexts development team to meet platform style, presentation, and quality:

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8.2: 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 $HCl(aq)$. When HCl is dissolved in H_2O, it completely **dissociates** (separates) into $H^+(aq)$ and $Cl^-(aq)$ ions; all the HCl molecules become ions:

$$HCl \overset{100\,\%}{\rightarrow} H^+(aq) + Cl^-(aq) \tag{8.2.1}$$

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:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq) \tag{8.2.2}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \tag{8.2.3}$$

As it turns out, there are very few strong acids, which are given in Table 8.2.1. 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 8.2.1: Some of the common strong acids and bases are listed here.

Strong Acids		Strong Bases	
$HClO_4$	perchloric acid	$LiOH$	lithium hydroxide
HCl	hydrochloric acid	$NaOH$	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	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 8.2.1); 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 8.2.1: 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 8.2.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 8.2.1, 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 8.2.1

Identify each acid or base as strong or weak.

a. RbOH
b. HNO_2

Answer

a. strong base
b. weak acid

✓ Example 8.2.2: 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:

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

Because $Ca(OH)_2$ is listed in Table 8.2.1, this reaction proceeds 100% to products.

? Exercise 8.2.2

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:

$$HN_3 \rightarrow H^+(aq) + N_3^-(aq)$$

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 [$HCl(aq)$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$HC_2H_3O_2(aq)$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is ammonia (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:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{8.2.4}$$

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 8.2.1: (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 equilibrium. For example, the ionization of the weak acid $HC_2H_3O_2(aq)$ is as follows:

$$HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq) \tag{8.2.5}$$

The reverse process also begins to occur:

$$H_3O^+(aq) + C_2H_3O_2^-(a \text{ [illegible] } HC_2H_3O_2(aq) + H_2O(\ell) \tag{8.2.6}$$

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:

$$HC_2H_3O_2(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq) \tag{8.2.7}$$

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 8.2.3: 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 8.2.3

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. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

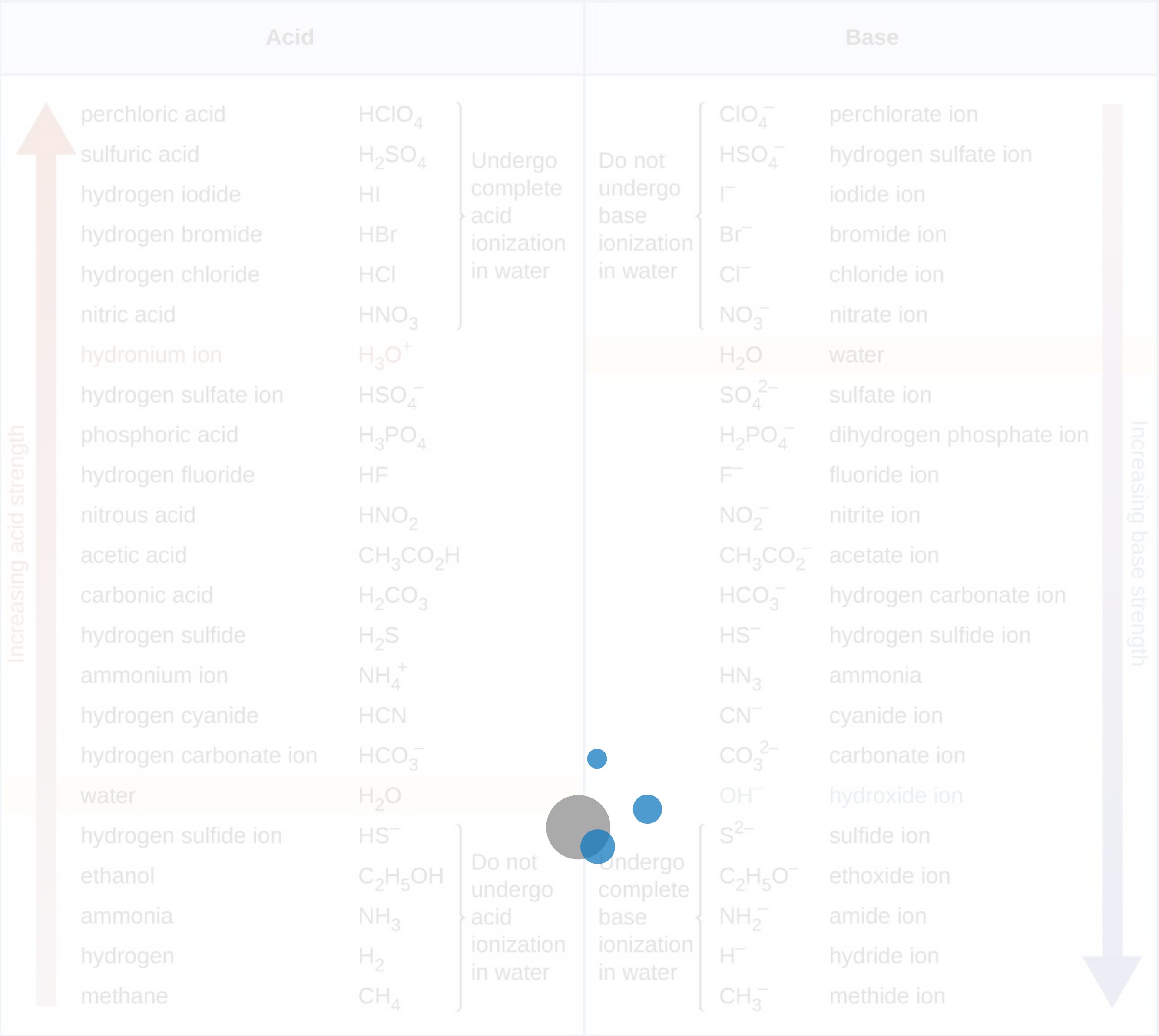
c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3{}^+(aq) + OH^-(aq)$

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, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure $8.2.2$).

The first six acids in Figure $8.2.2$ 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 $8.2.2$ 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 $8.2.2$ 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.



Acid				Base	
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			HN_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 8.2.2: 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 8.2.2. 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.

8.3: 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 $8.3.1$ 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.

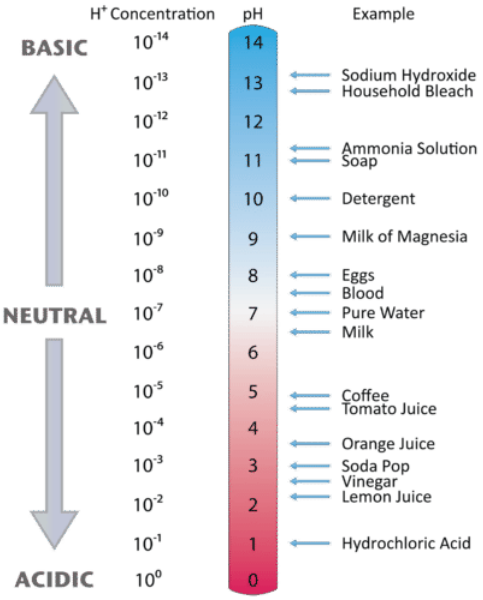


Figure $8.3.1$: The relationship between [H$^+$] and pH *values for several common materials.*

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 $8.3.1$: Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	[H$^+$] > [OH$^-$]	pH < 7

Classification	Relative Ion Concentrations	pH at 25°C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

✓ Example 8.3.1

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. $pH = - \log [\underline{1} \times 10^{-3}] = 3.\underline{0}$ (1 decimal place since 1 has 1 significant figure)
b. $pH = - \log [\underline{2.5} \times 10^{-11}] = 10.\underline{60}$ (2 decimal places since 2.5 has 2 significant figures)
c. $pH = - \log [\underline{4.7} \times 10^{-9}] = 8.\underline{33}$ (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 8.3.1

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 8.3.2 lists the pH of several common solutions. The most *aci*dic 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.

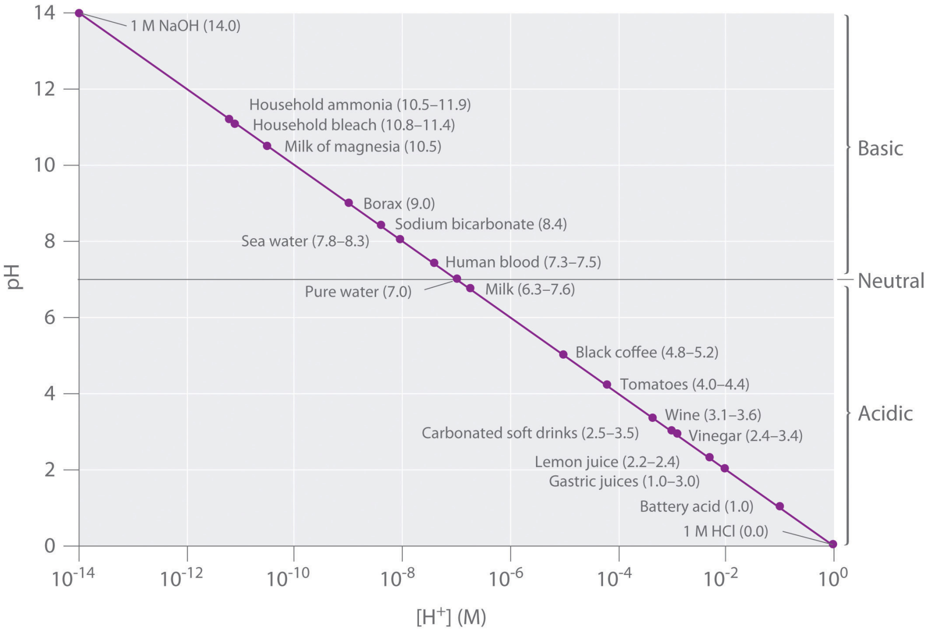


Figure 8.3.2: A Plot of pH versus $[H^+]$ for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

✓ Example 8.3.2

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 8.3.2

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 8.3.3)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 8.3.3).

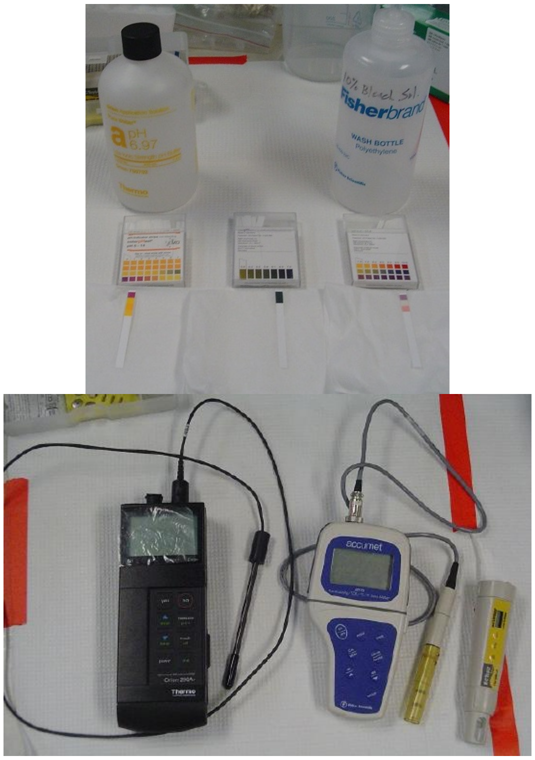


Figure 8.3.3: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center 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:

$$\mathrm{H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)} \tag{8.3.1}$$

$$\mathrm{H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{8.3.2}$$

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:

$$\mathrm{H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)} \tag{8.3.3}$$

$$\mathrm{H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)} \tag{8.3.4}$$

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 $8.3.4$). 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.

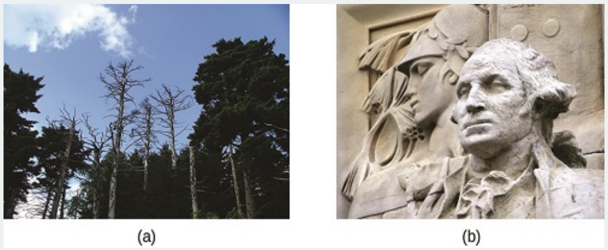


Figure $8.3.4$: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

8.4: Some Common Acid-Base Reactions

Maps take some time to build because we have to find or write matching materials. LibreTexts POV is that it is best to make available pages that we have finished rather than wait till the entire project is complete .This map is not completely finished, some pages are missing but we are workin' on it. . . (Public Domain ; Public Domain Pictures)

8.5: Buffer Solutions

Learning Objectives

- Describe the composition and function of acid–base buffers

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure $8.5.1$). A solution of acetic acid (CH_3COOH and sodium acetate CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3(aq)$) and ammonium chloride ($NH_4Cl(aq)$).

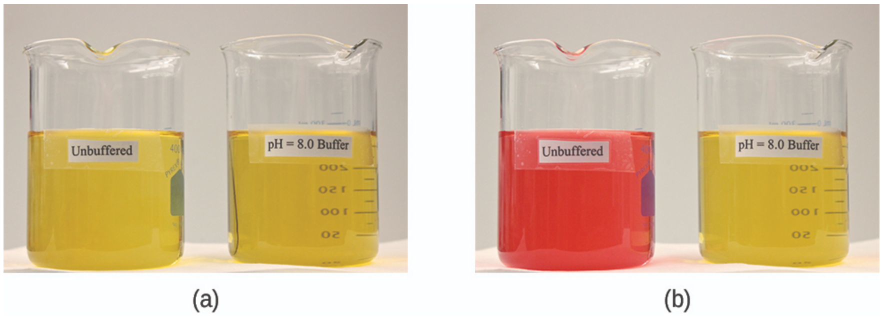


Figure $8.5.1$: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure $8.5.2$).

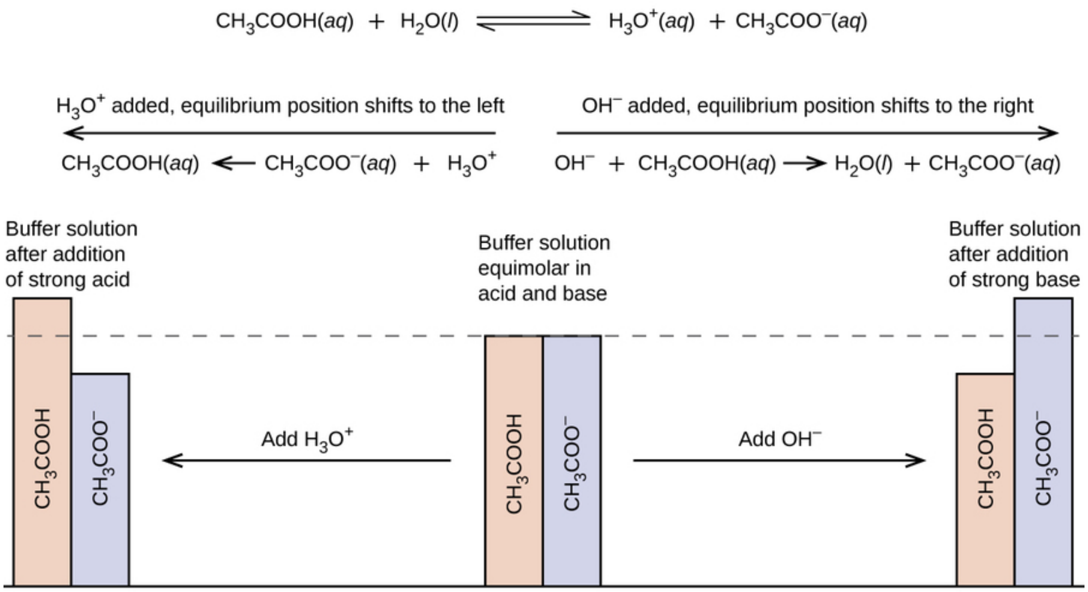


Figure 8.5.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 8.5.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.

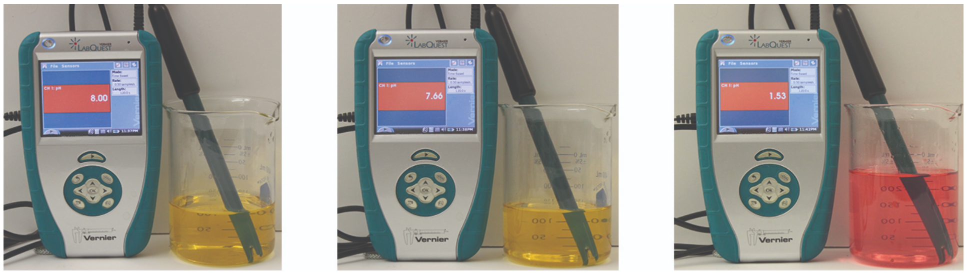


Figure 8.5.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$CO_2(g) + 2\,H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Glossary

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solution

8.6: Titration

Learning Objectives

- Describe a titration experiment.
- Explain what an indicator does.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure $8.6.1$). The burette has markings to determine how much volume of solution has been added to the analyte. When the reaction is complete, it is said to be at the **equivalence point**; the number of moles of titrant can be calculated from the concentration and the volume, and the balanced chemical equation can be used to determine the number of moles (and then concentration or mass) of the unknown reactant.

Figure 8.6.1 Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\text{\# mol HCl} = (0.02566\ \text{L})(0.1078\ \text{M}) = 0.002766\ \text{mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ mol\ \cancel{HCl} \times \frac{1\ mol\ NaOH}{1\ mol\ \cancel{HCl}} = 0.002766\ mol\ NaOH$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ mol\ \cancel{HCl} \times \frac{40.00\ g\ NaOH}{1\ mol\ \cancel{HCl}} = 0.1106\ g\ NaOH$$

This type of calculation is performed as part of a titration.

Example $8.6.1$

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO_3? The balanced chemical equation is as follows:

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

$$\text{\# moles } HNO_3 = (0.04402\ \text{L})(0.0885\ \text{M}) = 0.00390\ \text{mol } HNO_3$$

Using the balanced chemical equation, we can determine the number of moles of Ca(OH)$_2$ present in the analyte:

$$0.00390\ mol\,\cancel{HNO_3} \times \frac{1\,mol\,Ca(OH)_2}{2\ mol\,\cancel{HNO_3}} = 0.00195\,mol\,Ca(OH)_2$$

Then we convert this to a mass using the molar mass of Ca(OH)$_2$:

$$0.00195\ mol\,\cancel{Ca(OH)_2} \times \frac{74.1\,g\,Ca(OH)_2}{mol\,\cancel{Ca(OH)_2}} = 0.144\,g\,Ca(OH)_2$$

Exercise 8.6.1

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$\mathrm{H_2C_2O_4 + 2\,NaOH \rightarrow Na_2C_2O_4 + 2\,H_2O}$$

Answer

0.182 g

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes color depending on the acidity or basicity of the solution. Because different indicators change colors at different levels of acidity, choosing the correct one is important in performing an accurate titration.

CHAPTER OVERVIEW

9: Solids, Liquids, and Gases

Most of us are familiar with the three phases of matter: solid, liquid, and gas. Indeed, we addressed the energy changes involved in phase changes. The substance we are probably most familiar with has those three phases: water. In everyday life, we commonly come in contact with water as a solid (ice), as a liquid, and as a gas (steam). All we have to do is change the conditions of the substance—typically temperature—and we can change the phase from solid to liquid to gas and back again. Under the proper conditions of temperature and pressure, many substances—not only water—can experience the three different phases. An understanding of the phases of matter is important for our understanding of all matter. In this chapter, we will explore the three phases of matter.

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9.1: Prelude to Solids, Liquids, and Gases

We normally experience carbon dioxide (CO_2) as a gas, but if it were cooled down to about −78°C, it would become a solid. The everyday term for solid carbon dioxide is dry ice.

Why "dry" ice? Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves. The cold carbon dioxide gas is also heavier than air (because it is cold and more dense), so people in the presence of dry ice should be in a well-ventilated area.

Figure 9.1.1: Dry ice. (CC BY SA 3.0 unported; ProjectManhattan).

Dry ice has several common uses. Because it is so cold, it is used as a refrigerant to keep other things cold or frozen (e.g., meats or ice cream). In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It also has dermatological applications (e.g., freezing off warts). Organs for transplant are kept cool with dry ice until the recipient of the new organ is ready for surgery. In this respect, carbon dioxide is much like water—more than one phase of the same substance has significant uses in the real world.

9.2: Intermolecular Interactions

Learning Objectives

- Define *phase*.
- Identify the types of interactions between molecules.

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 8.1.1). Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

> *For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.*

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 9.2.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 9.2.1: Temperature Ranges for the Three Phases of Various Substances

Substance	Solid Phase Below	Liquid Phase Above	Gas Phase Above
hydrogen (H_2)	−259°C	−259°C	−253°C
water (H_2O)	0°C	0°C	100°C
sodium chloride (NaCl)	801°C	801°C	1413°C

The *melting point* of a substance is the temperature that separates a solid and a liquid. The *boiling point* of a substance is the temperature that separates a liquid and a gas.

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

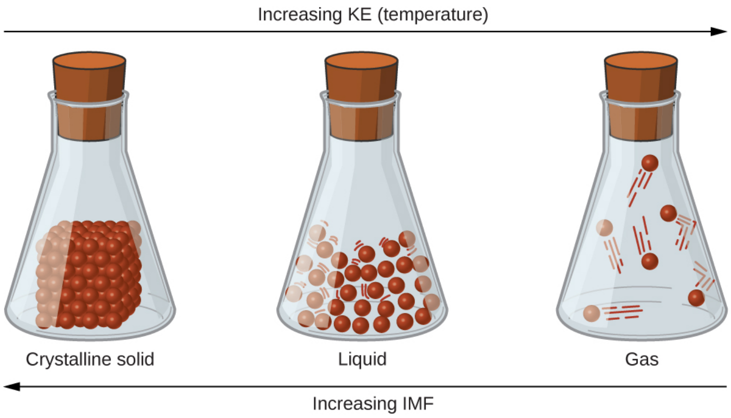

Figure 9.2.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

Three sealed flasks are labeled, “Crystalline solid,” “Liquid,” and “Gas,” from left to right. The first flask holds a cube composed of small spheres sitting on the bottom while the second flask shows a lot of small spheres in the bottom that are spaced a small distance apart from one another and have lines around them to indicate motion. The third flask shows a few spheres spread far from one another with larger lines to indicate motion. There is a right-facing arrow that spans the top of all three flasks. The arrow is labeled, “Increasing K E (temperature).” There is a left-facing arrow that spans the bottom of all three flasks. The arrow is labeled, “Increasing I M F.”

Covalent Network Materials

Substances with the highest melting and boiling points have **covalent network** bonding. This type of intermolecular interaction is actually a covalent bond. In these substances, all the atoms in a sample are covalently bonded to one another; in effect, the entire sample is essentially **one giant molecule**. Many of these substances are solid over a large temperature range because it takes a lot of energy to disrupt all the covalent bonds at once. One example of a substance that shows covalent network bonding is diamond (Figure 9.2.2). 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 3,500°C. Diamond is extremely hard and is one of the few materials that can cut glass.

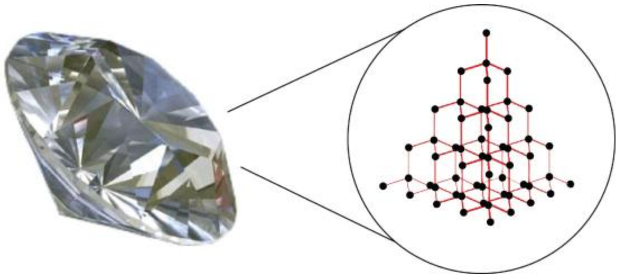

Figure 9.2.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

Ionic Compounds

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 9.2.3) is an example of a substance whose particles experience ionic interactions (Table 9.2.1). These attractive forces are sometimes referred to as ion-ion interactions.

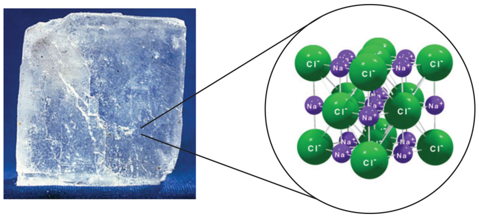

Figure 9.2.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

Covalent Molecular Compounds

There are two different covalent structures: molecular and network. Covalent network compounds like SiO_2 (quartz) have structures of atoms in a network like diamond described earlier. In this section, we are dealing with the molecular type that contains individual molecules. The bonding between atoms in the individual molecule is covalent but the attractive forces between the molecules are called ***intermolecular forces (IMF)***.

In contrast to *intramolecular* forces (see Figure 8.1.4), such as the covalent bonds that hold atoms together in molecules and polyatomic ions, intermolecular forces hold molecules together in a **liquid or solid**. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances ***without breaking covalent bonds.***

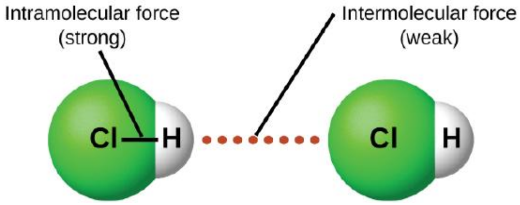

Figure 9.2.4: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties.

In this section, we will discuss the three types of IMF in molecular compounds: dipole-dipole, hydrogen bonding and London dispersion forces.

Dipole-dipole Intermolecular Forces

As discussed in Section 4.4, covalent bond that has an unequal sharing of electrons is called a **polar covalent** bond. (A covalent bond that has an equal sharing of electrons, as in a covalent bond with the same atom on each side, is called a **nonpolar covalent** bond.) A molecule with a net unequal distribution of electrons in its covalent bonds is a polar molecule. HF is an example of a polar molecule (see Figure 8.1.5).

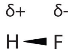

Figure 9.2.5: Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ− in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ+ in the diagram). Such a bond is called a *polar covalent bond*.

The charge separation in a **polar covalent bond** is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a **dipole-dipole interaction**. Many molecules with polar covalent bonds experience dipole-dipole interactions.

The covalent bonds in some molecules are oriented in space in such a way that the bonds in the molecules cancel each other out. The individual bonds are polar, but due to molecular symmetry, the overall molecule is not polar; rather, the molecule is ***nonpolar.*** Such molecules experience little or no dipole-dipole interactions. Carbon dioxide (CO_2) and carbon tetrachloride (CCl_4) are examples of such molecules (Figure 9.2.6).

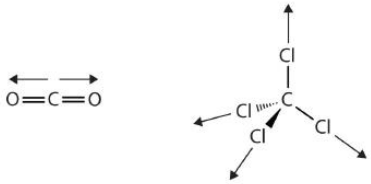

Figure 9.2.6: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

Recall from the Sections 4.4 and 4.5, on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole.*** Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 9.2.7.

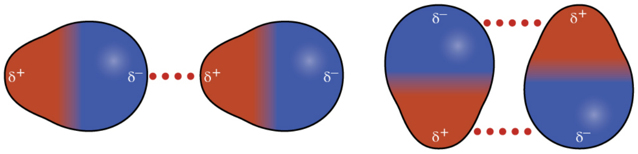

Figure 9.2.7: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Two pairs of molecules are shown where each molecule has one larger blue side labeled “delta sign, negative sign” and a smaller red side labeled “delta sign, positive sign. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends aligning. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average kinetic energy. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points as indicators of the relative strengths of IMFs of attraction present within different substances.

✓ Example 9.2.1

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

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

Answer

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

Hydrogen Bonding Intermolecular Forces

Molecules with **hydrogen atoms** bonded to electronegative atoms such as **O, N, and F** tend to exhibit unusually strong intermolecular interactions due to a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to ***highly concentrated partial charges*** with these atoms. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

Examples of hydrogen bonds include HF⋯HF, $H_2O\cdots HOH$, and $H_3N\cdots HNH_2$, in which the **hydrogen bonds** are denoted by **dots**. Figure 9.2.8 illustrates hydrogen bonding between water molecules. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state.

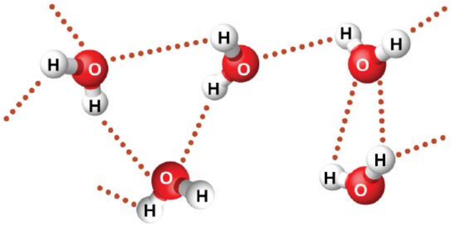


Figure 9.2.8: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

A **hydrogen bond** is an intermolecular attractive force in which *a* **hydrogen atom**, that is covalently bonded to a small, highly electronegative atom, is attracted to a **lone pair of electrons** on an atom in a neighboring molecule. Figure 9.2.9 shows how methanol (CH_3OH) molecules experience hydrogen bonding. Methanol contains both a hydrogen atom attached to O; methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor (lone pair). The hydrogen-bonded structure of methanol is as follows:

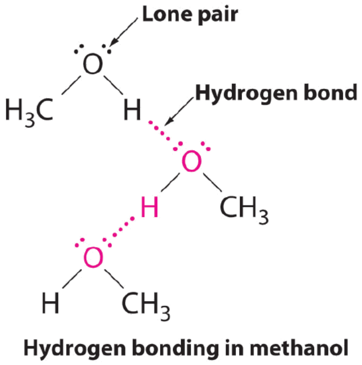


Figure 9.2.9: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

✓ Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

? Exercise 9.2.2

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

> The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 9.2.10.

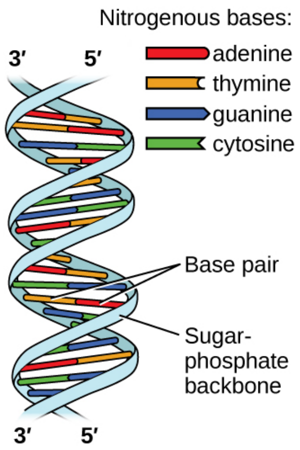


Figure 9.2.10: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Two images are shown. The first lies on the left side of the page and shows a helical structure like a twisted ladder where the rungs of the ladder, labeled “Base pair” are red, yellow, green and blue paired bars. The red and yellow bars, which are always paired together, are labeled in the legend, which is titled “Nitrogenous bases” as “adenine” and “thymine,” respectively. The blue and green bars, which are always paired together, are labeled in the legend as “guanine” and “cytosine,” respectively. At the top of the helical structure, the left-hand side rail, or “Sugar, dash, phosphate backbone,” is labeled as “3, prime” while the right is labeled as “5, prime.” These labels are reversed at the bottom of the helix. To the right of the page is a large Lewis structure. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 9.2.11

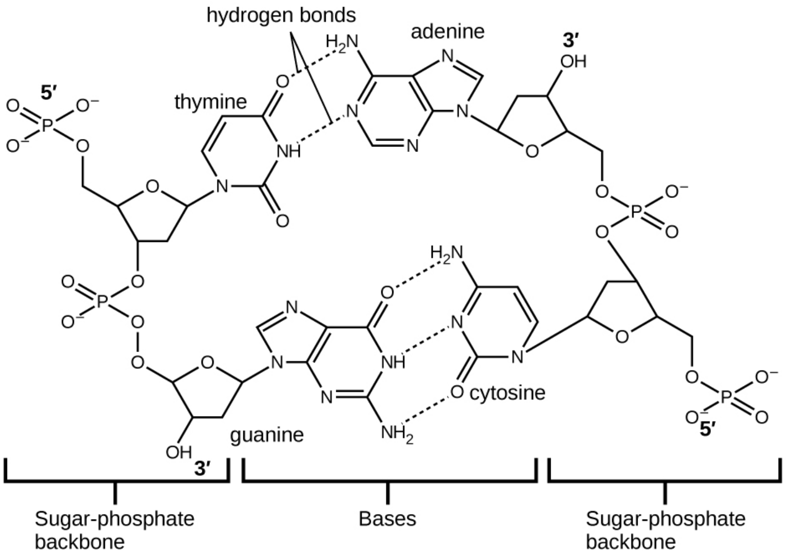


Figure 9.2.11: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

A large Lewis structure is shown. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

London Dispersion Forces

Finally, there are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge that disappears almost as soon as it appears. These are very weak intermolecular interactions and are called **dispersion forces (or London forces)**. (An alternate name is London dispersion forces.) Molecules that experience no other type of intermolecular interaction will at least experience dispersion forces. Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.1.2.

Table 9.2.2: **Melting and Boiling Points of the Halogens**

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

✓ Example 9.2.3

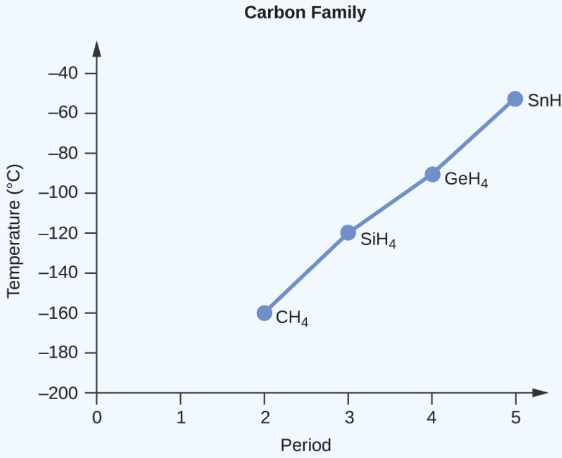
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

A graph of the actual boiling points of these compounds versus the period of the group 14 elementsshows this prediction to be correct:



A line graph, titled “Carbon Family,” is shown where the y-axis is labeled “Temperature, (degree sign C)” and has values of “negative 200” to “negative 40” from bottom to top in increments of 20. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. The first point on the graph is labeled “C H subscript 4” and is at point “2, negative 160.” The second point on the graph is labeled “S i H subscript 4” and is at point “3, negative 120” while the third point on the graph is labeled “G e H subscript 4” and is at point “4, negative 100.” The fourth point on the graph is labeled “S n H subscript 4” and is at point “5, negative 60.”

rcise

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

Answer

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

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

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos’ feet to behave this way.

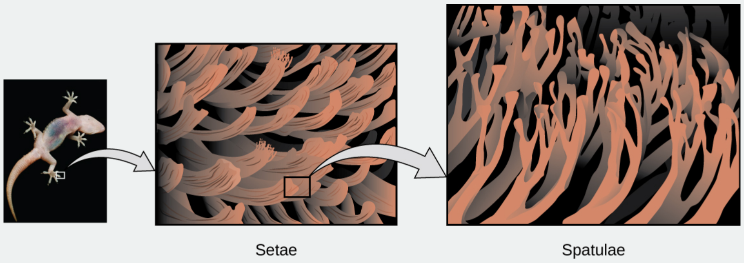


Figure 9.2.12: *Geckos’ toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko’s millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness “on” and “off.” (credit photo: modification of work by “JC*+A!”/Flickr)*

Three figures are shown. The first is a photo of the bottom of a gecko’s foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

Geckos’ toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 9.2.3: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61
NH_3	hydrogen bonding	-33
HF	hydrogen bonding	20
H_2O	hydrogen bonding	100

✓ Example 9.2.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)

c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

? Exercise 9.2.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

9.3: Solids and Liquids

Learning Objectives

- To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

Solids

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

Figure $9.3.1$: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure $9.3.1$. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

Liquids

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

Figure $9.3.2$: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. from Wikipedia.

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

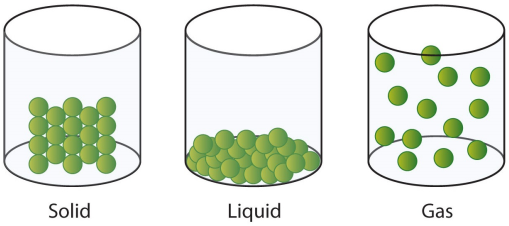


Figure $9.3.3$: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure $9.3.3$ shows the differences among solids, liquids, and gases at the molecular level, while Table $9.3.1$ lists the different characteristics of these states.

Table $9.3.1$: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

✓ Example $9.3.1$

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

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

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

? Exercise $9.3.1$

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
b. gas
c. solid

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

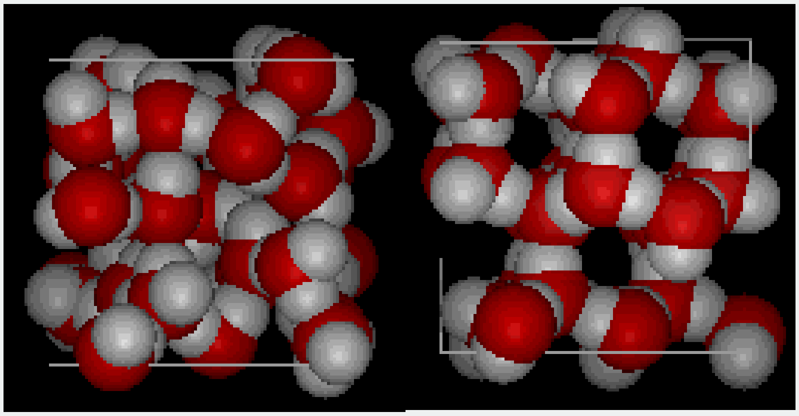


Figure 9.3.4: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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9.4: Gases and Pressure

Learning Objectives

- To describe the gas phase.

The gas phase is unique among the three states of matter in that there are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. In fact, the development of this understanding of the behavior of gases represents the historical dividing point between alchemy and modern chemistry. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

How is it that we can model all gases independent of their chemical identity? The answer is in a group of statements called the kinetic theory of gases:

- Gases are composed of tiny particles that are separated by large distances.
- Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container.
- The velocity of gas particles is related to the temperature of a gas.
- Gas particles do not experience any force of attraction or repulsion with each other.

Did you notice that none of these statements relates to the identity of the gas? This means that all gases should behave similarly. A gas that follows these statements perfectly is called an *ideal gas*. Most gases show slight deviations from these statements and are called *real gases*. However, the existence of real gases does not diminish the importance of the kinetic theory of gases.

One of the statements of the kinetic theory mentions collisions. As gas particles are constantly moving, they are also constantly colliding with each other and with the walls of their container. There are forces involved as gas particles bounce off the container walls (Figure 9.4.1). The force generated by gas particles divided by the area of the container walls yields pressure. Pressure is a property we can measure for a gas, but we typically do not consider pressure for solids or liquids.

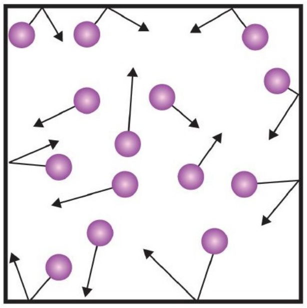


Figure 9.4.1: Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.

The basic unit of pressure is the newton per square meter (N/m^2). This combined unit is redefined as a pascal (Pa). One pascal is not a very large amount of pressure. A more useful unit of pressure is the bar, which is 100,000 Pa (1 bar = 100,000 Pa). Other common units of pressure are the atmosphere (atm), which was originally defined as the average pressure of Earth's atmosphere at sea level; and mmHg (millimeters of mercury), which is the pressure generated by a column of mercury 1 mm high. The unit millimeters of mercury is also called a torr, named after the Italian scientist Evangelista Torricelli, who invented the barometer in the mid-1600s. A more precise definition of atmosphere, in terms of torr, is that there are exactly 760 torr in 1 atm. A bar equals 1.01325 atm. Given all the relationships between these pressure units, the ability to convert from one pressure unit to another is a useful skill.

✓ Example 9.4.1: Converting Pressures

Write a conversion factor to determine how many atmospheres are in 1,547 mmHg.

Solution

Because 1 mmHg equals 1 torr, the given pressure is also equal to 1,547 torr. Because there are 760 torr in 1 atm, we can use this conversion factor to do the mathematical conversion:

$$1,547\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 2.04\ \text{atm}$$

Note how the torr units cancel algebraically.

? Exercise 9.4.1: Converting Pressures

Write a conversion factor to determine how many millimeters of mercury are in 9.65 atm.

Answer

$$9.65\ \text{atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 7,334\ \text{mmHg}$$

The kinetic theory also states that there is no interaction between individual gas particles. Although we know that there are, in fact, intermolecular interactions in real gases, the kinetic theory assumes that gas particles are so far apart that the individual particles don't "feel" each other. Thus, we can treat gas particles as tiny bits of matter whose identity isn't important to certain physical properties.

Key Takeaway

- The gas phase has certain general properties characteristic of that phase.

9.5: Gas Laws

Learning Objectives

- To predict the behavior of gases using the gas laws.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (*P*), volume (*V*), temperature (*T*, in kelvins), and amount of material expressed in moles (*n*). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

Boyle's Law

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$\mathrm{P} \propto \frac{1}{\mathrm{V}}$$

where the "∝" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{9.5.1}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 9.5.1, you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

✓ Example 9.5.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

Solution

If the pressure of a gas is increased, the volume decreases in response.

? Exercise 9.5.1: Increasing Volume in a Gas

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Answer

If the volume of a gas is increased, the pressure decreases.

✓ Example 9.5.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

Solution

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56\text{ atm})(7.02\text{ L}) = (0.987\text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02\text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02\text{ L})}{0.987} = \text{V}_\text{f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

? Exercise 9.5.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

Answer

8.48 atm

? Exercise 9.5.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4.577 L? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

Answer

575 torr

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

Charles's Law

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant. The way to write this mathematically is

$$\mathrm{V} \propto T$$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

Kelvin temperature = Celsius temperature + 273

Thus, it is easy to convert from one temperature scale to another.

> The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is −260°C or −459°F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

✓ Example 9.5.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

Solution

If the temperature of a gas sample is decreased, the volume decreases as well.

? Exercise 9.5.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

Answer

The temperature increases.

Combined Gas Law

Other gas laws can be constructed, but we will focus on only two more. The combined gas law brings Boyle's and Charles's laws together to relate pressure, volume, and temperature changes of a gas sample:

$$\frac{\mathrm{P_i V_i}}{\mathrm{T_i}} = \frac{\mathrm{P_f V_f}}{\mathrm{T_f}}$$

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

✓ Example 9.5.6

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

Solution

Using the combined gas law, substitute for five of the quantities:

$$\frac{(1.50\ \mathrm{atm})(10.5\ \mathrm{L})}{300\ \mathrm{K}} = \frac{(0.750\ \mathrm{atm})(\mathrm{V_f})}{350\ \mathrm{K}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$V_f = \frac{(1.50\ \text{atm})(10.5\ \text{L})(350\ \text{K})}{(300\ \text{K})(0.750\ \text{atm})} = 24.5\ \text{L}$$

Note how all the units cancel except the unit for volume.

rcise

A sample of gas has P_i = 0.768 atm, V_i = 10.5 L, and T_i = 300 K. What is the final pressure if V_f = 7.85 L and T_f = 250 K?

Answer

0.856 atm

✓ Example 9.5.7

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

Solution

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22°\text{C} + 273 = 295\ \text{K} = T_i$$

$$11°\text{C} + 273 = 284\ \text{K} = T_f$$

$$1.09\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 828\ \text{torr} = P_i$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})}{295\ \text{K}} = \frac{(655\ \text{torr}) \times V_f}{284\ \text{K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})(284\ \text{K})}{(295\ \text{K})(655\ \text{torr})} = V_f$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

rcise

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of −15°C. What is the new volume of the gas?

Answer

110,038 L

The Ideal Gas Law

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT$$

In this equation, P is pressure, V is volume, n is amount of moles, and T is temperature. R is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts *i* and *f* to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of R depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of R is as follows:

$$\mathrm{R} = 0.08205\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

✓ **Example 9.5.8**

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

Solution

Using the ideal gas law where P = 3.995 atm, n = 1.45, and T = 298,

$$(3.995\ \mathrm{atm}) \times \mathrm{V} = (1.45\ \mathrm{mol}) \left(0.08205\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}}\right) (298\ \mathrm{K})$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298)\ \mathrm{L}$$

Dividing both sides of the equation by 3.995 and evaluating, we get V = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

rcise

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

Answer

1.03 atm

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00\ \mathrm{atm}) \times \mathrm{V} = (1.00\ \mathrm{mol}) \left(0.08205\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}}\right) (273\ \mathrm{K})$$

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

$$1\ \text{mol gas} = 22.4\ \text{L (at STP)}$$

✓ **Example 9.5.9**

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

Solution

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0\ \mathrm{L\ C_3H_6} \times \frac{1\ \mathrm{mol}}{22.4\ \mathrm{L}} = 4.46\ \mathrm{mol\ C_3H_6}$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

rcise

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

Answer

196 L

Airbags

Airbags (Figure 9.5.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,\mathrm{NaN_3}(s) \rightarrow 3\,\mathrm{N_2}(g) + 2\,\mathrm{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.

Figure 9.5.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. The only new concept we need in order to deal with gas mixtures is the *partial pressure*. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 \ldots = \sum_i P_i$$

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 (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + \ldots + P_n$$

or

$$P_n = \frac{\%\text{ of individual gas}_n}{P_{Total}}$$

Table 9.5.1: 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.

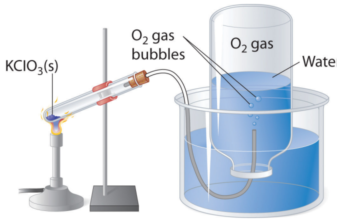


Figure 9.5.1:An Apparatus for Collecting Gases by the Displacement of Water

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.

Career Focus: Respiratory Therapist

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate’s degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor’s offices, nursing homes, or patient’s homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

9.E: Solids, Liquids, and Gases (Exercises)

Intermolecular Interactions

Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.
2. List the three common phases in the order they exist from lowest energy to highest energy.
3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.
4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.
5. What type of intermolecular interaction is predominate in each substance?
   a. water (H_2O)
   b. sodium sulfate (Na_2SO_4)
   c. decane ($C_{10}H_{22}$)
6. What type of intermolecular interaction is predominate in each substance?
   a. diamond (C, crystal)
   b. helium (He)
   c. ammonia (NH_3)
7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
   b. ionic interactions
   c. dispersion forces

6. a. network covalent
b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

Solids and Liquids

Concept Review Exercise

1. How do the strengths of intermolecular interactions in solids and liquids differ?

Answer

1. Solids have stronger intermolecular interactions than liquids do.

Exercises

1. What are the general properties of solids?
2. What are the general properties of liquids
3. What are the general properties of gases?
4. What phase or phases have a definite volume? What phase or phases do not have a definite volume?
5. Name a common substance that forms a crystal in its solid state.
6. Name a common substance that forms an amorphous solid in its solid state.
7. Are substances with strong intermolecular interactions likely to be solids at higher or lower temperatures? Explain.
8. Are substances with weak intermolecular interactions likely to be liquids at higher or lower temperatures? Explain.
9. State two similarities between the solid and liquid states.
10. State two differences between the solid and liquid states.
11. If individual particles are moving around with respect to each other, a substance may be in either the _______ or ________ state but probably not in the _______ state.
12. If individual particles are in contact with each other, a substance may be in either the ______ or _______ state but probably not in the ______ state.

Answers

1. hard, specific volume and shape, high density, cannot be compressed

2. fixed volume, no definite shape, high density, individual molecules touch each other but in a random way

3. variable volume and shape, low density, compressible

4. solid and liquid have definite volume; gas has no definite volume

5. sodium chloride (answers will vary)

6. glass

7. At higher temperatures, their intermolecular interactions are strong enough to hold the particles in place.

8. Substances with weak intermolecular interactions are likely to be liquids at lower temperatures. Their attractive forces are more easily broken hence they melt more readily.

9. high density; definite volume

10. Solids have definite shape while liquids don't. In solids, molecules occupy fixed positions in a pattern, while in liquids, the molecules are moving in a random arrangement.

11. liquid; gas; solid

12. solid; liquid; gas

8.3: Gases and Pressure

Concept Review Exercise

1. What is pressure, and what units do we use to express it?

Answer

1. Pressure is the force per unit area; its units can be pascals, torr, millimeters of mercury, or atmospheres.

Exercises

1. What is the kinetic theory of gases?
2. According to the kinetic theory of gases, the individual gas particles are (always, frequently, never) moving.
3. Why does a gas exert pressure?
4. Why does the kinetic theory of gases allow us to presume that all gases will show similar behavior?

Answers

1. Gases are composed of tiny particles that are separated by large distances. Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container. The velocity of gas particles is related to the temperature of a gas. Gas particles do not experience any force of attraction or repulsion with each other.

2. always

3. A gas exerts pressure as its particles rebound off the walls of its container.

4. Because the molecules are far apart and don't have attractive forces between them

8.4: Gas Laws

Concept Review Exercises

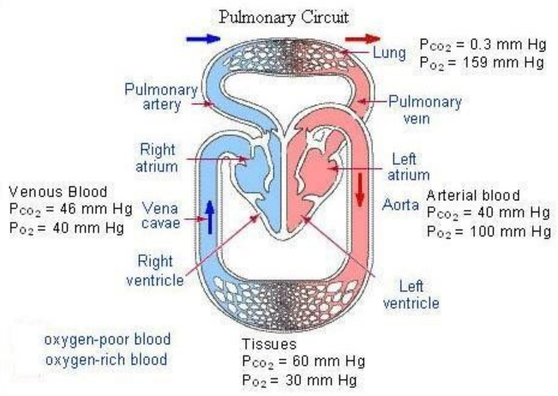
1. What properties do the gas laws help us predict?
2. What makes the ideal gas law different from the other gas laws?

Answers

1. Gas laws relate four properties: pressure, volume, temperature, and number of moles.
2. The ideal gas law does not require that the properties of a gas change.

Exercises

1. A sample of nitrogen gas is confined to a balloon that has a volume of 1.88 L and a pressure of 1.334 atm. What will be the volume of the balloon if the pressure is changed to 0.662 atm? Assume that the temperature and the amount of the gas remain constant.
2. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.
3. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?
4. What must V be for a gas sample if n = 4.55 mol, P = 7.32 atm, and T = 285 K?
5. Apply Henry’s Law to the diagram below to explain: a) why oxygen diffuses from the alveoli of the lungs into the blood and from the blood into the tissues of the body. b) why carbon dioxide diffuses from the tissues into the blood and from the blood into the alveoli and then finally out into the atmosphere.



Answers

1. 3.79 L
2. The ideal gas law confirms that 22.4 L equals 1 mol.
3. 1.63 mol
4. 14.5 L
5. Gases diffuse from high concentration to low concentration (Henry's Law). The partial pressure of **oxygen** is high in the **alveoli** and low in the **blood** of the pulmonary capillaries. As a result, **oxygen diffuses** across the respiratory membrane from the **alveoli** into the **blood**. It's also higher partial pressure in the blood than in the tissues, hence it transfers to the tissues. On the other hand, carbon dioxide **diffuses** from the tissues (highest CO_2 partial pressure) and across the respiratory membrane from the **blood** into the **alveoli** and out **to the atmosphere.**

9.S: Solids, Liquids, and Gases (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A **phase** is a certain form of matter that has the same physical properties throughout. Three phases are common: the solid, the liquid, and the gas phase. What determines the phase of a substance? Generally, the strength of the **intermolecular interactions** determines whether a substance is a solid, liquid, or gas under any particular conditions. **Covalent network bonding** is a very strong form of intermolecular interaction. Diamond is one example of a substance that has this intermolecular interaction. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong. Covalent bonds are another type of interaction within molecules, but if the bonds are **polar covalent bonds**, then the unequal sharing of electrons can cause charge imbalances within molecules that cause interactions between molecules. These molecules are described as **polar**, and these interactions are called **dipole-dipole interactions**. A certain rather strong type of dipole-dipole interaction, involving a hydrogen atom, is called **hydrogen bonding**. On the other hand, equal sharing of electrons forms **nonpolar covalent bonds**, and the interactions between different molecules is less because the molecules are nonpolar. All substances have very weak **dispersion forces** (also called **London forces**) caused by the movement of electrons within the bonds themselves.

In the solid phase, intermolecular interactions are so strong that they hold the individual atoms or molecules in place. In many solids, the regular three-dimensional arrangement of particles makes a **crystal**. In other solids, the irregular arrangement of particles makes an **amorphous** solid. In liquids, the intermolecular interactions are strong enough to keep the particles of substance together but not in place. Thus, the particles are free to move over each other but still remain in contact.

In gases, the intermolecular interactions are weak enough that the individual particles are separated from each other in space. The **kinetic theory of gases** is a collection of statements that describe the fundamental behavior of all gases. Among other properties, gases exert a **pressure** on their container. Pressure is measured using units like **pascal**, **bar**, **atmosphere**, or **mmHg** (also called a **torr**).

There are several simple relationships between the variables used to describe a quantity of gas. These relationships are called **gas laws**. **Boyle's law** relates the pressure and volume of a gas, while **Charles's law** relates the volume and absolute temperature of a gas. The **combined gas law** relates the volume, pressure, and absolute temperature of a gas sample. All of these gas laws allow us to understand the changing conditions of a gas. The **ideal gas law** relates the pressure, volume, amount, and absolute temperature of a gas under any conditions. These four variables are related to the **ideal gas law constant**, which is the proportionality constant used to calculate the conditions of a gas. Because the conditions of a gas can change, a set of benchmark conditions called **standard temperature and pressure (STP)** is defined. Standard temperature is 0ºC, and standard pressure is 1.00 atm.

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CHAPTER OVERVIEW

10: Alkanes, Cycloalkanes, and Halogenated Alkanes

10.1: The Nature of Organic Molecules

Learning Objectives

- Describe the basic structural properties of simple organic molecules.

Organic chemistry is the study of the chemistry of carbon-containing compounds. Carbon is singled out because it has a chemical diversity unrivaled by any other chemical element. Its diversity is based on the following:

- Carbon atoms bond reasonably strongly with other carbon atoms.
- Carbon atoms bond reasonably strongly with atoms of other elements.
- Carbon atoms make a large number of covalent bonds (four).

Curiously, elemental carbon is not particularly abundant. It does not even appear in the list of the most common elements in Earth's crust. Nevertheless, all living things consist of organic compounds. Most organic chemicals are covalent compounds, which is why we introduce organic chemistry here. By convention, compounds containing carbonate ions and bicarbonate ions, as well as carbon dioxide and carbon monoxide, are not considered part of organic chemistry, even though they contain carbon.

Structural Properties of Carbon Compounds

A carbon atom has four valence electrons, it is **tetravalent**. Carbon can form four *covalent* bonds, or *share electrons with* up to four atoms in order to gain a complete octet. The simplest carbon compounds contain only carbon and hydrogen and are called **hydrocarbons**. Methane, the simplest hydrocarbon, contains a single carbon with four covalently bonded hydrogen atoms. Recalling what you have learned about molecular structures and VSEPR, we know that methane is **tetrahedral** (four electron groups and no lone pairs).

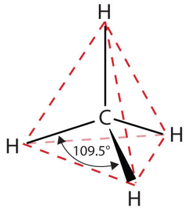


Figure 10.1.1: The Tetrahedral Methane Molecule

Carbon can also form **double bonds** by sharing *four electrons* with a neighboring carbon atom or **triple bonds** by sharing *six electrons* with a neighboring carbon atom. As shown in Figure 10.1.2 below, carbon with three electron groups attached will be **trigonal planar**, and carbon with two electron groups attached will be **linear**.

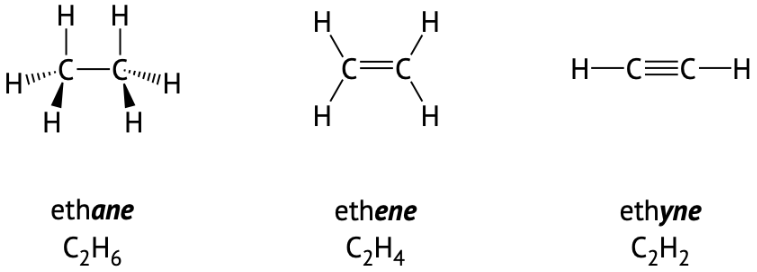


Figure 10.1.2: Two carbons can be attached together in single bond, a double bond, or a triple bond. Notice, in each example carbon makes four total bonds. The number of hydrogen atoms in each molecule decreases as the number of carbon–carbon bonds increase.

Simple hydrocarbon compounds are *nonpolar* due to the shape and the small electronegativity difference between carbon and hydrogen atoms. When carbon is bonded to a halogen or oxygen atom, the resulting bond is *polar*. It may be useful to review the section on electronegativity and polarity of bonds and molecules to be able to describe the properties of different organic compounds, specifically how they react and interact with other molecules.

Comparing Organic and Inorganic Compounds

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 10.1.1. Keep in mind, however, that there are exceptions to every category in this table.

Table 10.1.1: Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic Properties	**Example:** Hexane	**Inorganic Properties**	**Example:** 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

---

10.2: Families of Organic Molecules - Functional Groups

Learning Objectives

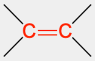
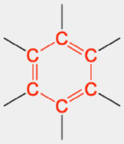
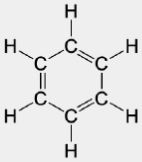
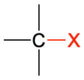
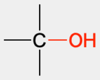
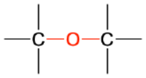
- Identify and describe functional groups in organic molecules.

Organic molecules can be classified into *families* based on structural similarities. Within a family, molecules have similar physical behavior and often have predictable chemical reactivity. The structural components differentiating different organic families involve specific arrangements of atoms or bonds, called **functional groups**. If you understand the behavior of a particular functional group, you can describe the general properties of that class of compounds.

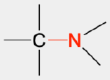
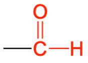
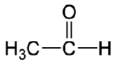
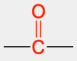
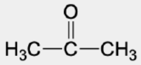
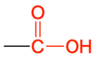
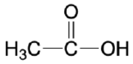
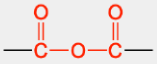
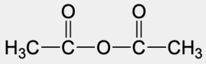
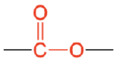
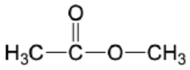
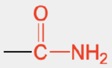
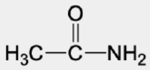
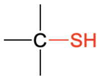
The simplest organic compounds are in the **alkane** family and contain only carbon–carbon and carbon–hydrogen *single* bonds but do not have any specific functional group. Hydrocarbons containing at least one carbon–carbon double bond, (denoted C=C), are in the **alkene** family. **Alkynes** have at least one carbon–carbon triple bond (C≡C). Both carbon–carbon double bonds and triple bonds chemically react in specific ways that differ from reactions of alkanes and each other, making these specific functional groups.

In the next few chapters, we will learn more about additional functional groups that are made up of atoms or groups of atoms attached to hydrocarbons. Being able to recognize different functional groups will help to understand and describe common medications and biomolecules such as amino acids, carbohydrates, and fats. Table 10.2.1 and Figure 10.2.1 below list several of the functional groups to become familiar with as you learn about organic chemistry.

Table 10.2.1: Organic Families and Functional Groups

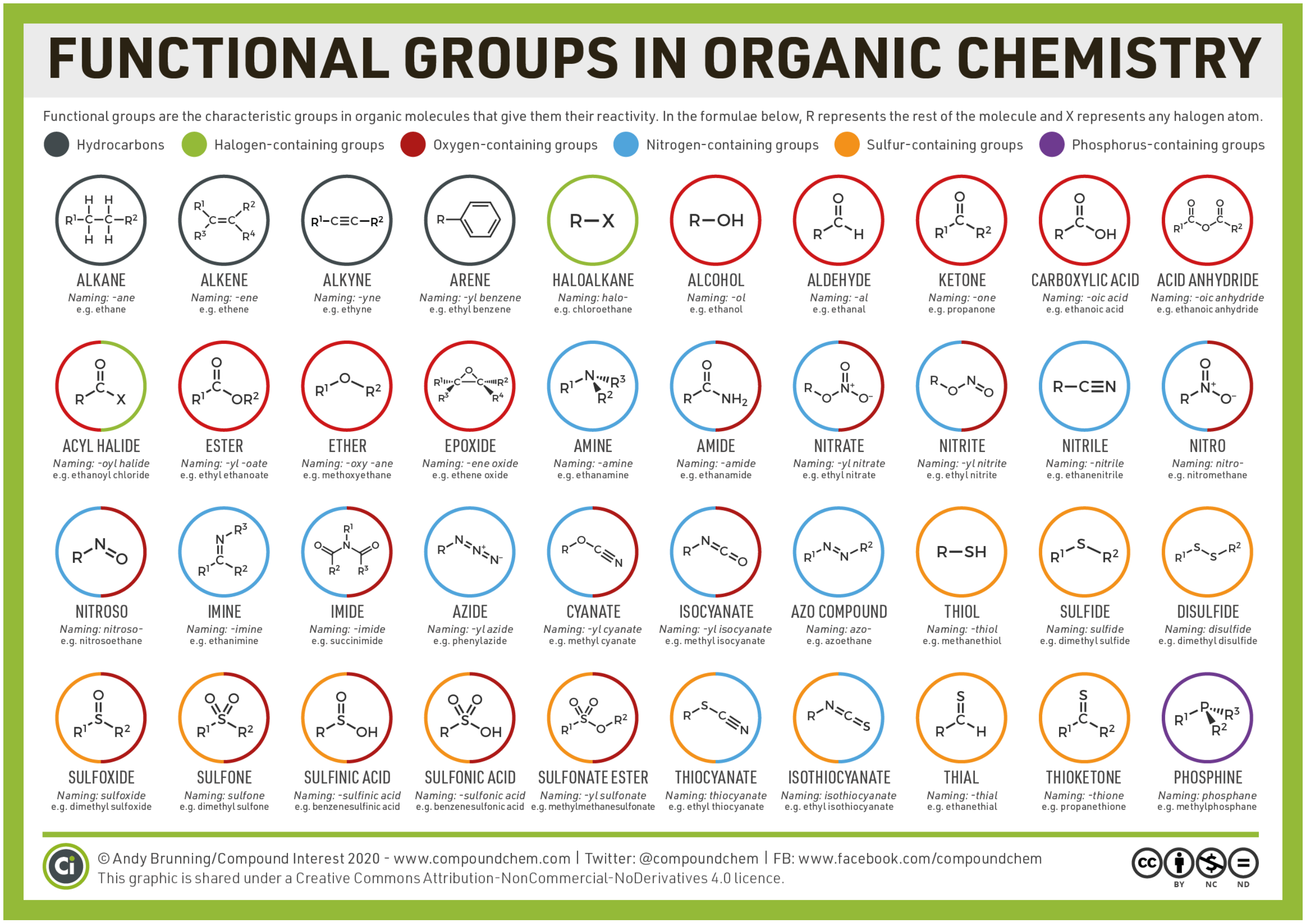
Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name	Name Suffix
alkane	none	$CH_3CH_2CH_3$	propane	-*ane*
alkene		$H_2C{=}CH_2$	ethene (ethylene)	-*ene*
alkyne		$HC{\equiv}CH$	ethyne (acetylene)	-*yne*
aromatic			benzene	none
alkyl halide	 (X = F, Cl, Br, I)	CH_3CH_2Cl	chloroethane	none
alcohol		CH_3CH_2OH	ethanol	-*ol*
ether		$CH_3CH_2{-}O{-}CH_2CH_3$	diethyl ether	none*

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hydrogens).
*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name	Name Suffix
amine		$CH_3CH_2NH_2$	ethylamine	*-amine*
aldehyde	 $-C(=O)-H$	 $H_3C-C(=O)-H$	ethanal	*-al*
ketone	 $-C(=O)-$	 $H_3C-C(=O)-CH_3$	propanone (acetone)	*-one*
carboxylic acid	 $-C(=O)-OH$	 $H_3C-C(=O)-OH$	ethanoic acid (acetic acid)	*-oic acid*
anhydride	 $-C(=O)-O-C(=O)-$	 $H_3C-C(=O)-O-C(=O)-CH_3$	acetic anhydride	none
ester	 $-C(=O)-O-$	 $H_3C-C(=O)-O-CH_3$	methyl ethanoate (methyl acetate)	*-ate*
amide	 $-C(=O)-NH_2$	 $H_3C-C(=O)-NH_2$	acetamide	*-amide*
thiol		CH_3CH_2SH	ethanethiol	*-thiol*
disulfide	$-S-S-$	$CH_3S–SCH_3$	dimethyl disulfide	none
sulfide	$-S-$	$CH_3CH_2SCH_3$	ethyl methyl sulfide	none

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hydrogens).
*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Organic-Functional-Groups-2016_24ee.pdfOrganic-Functional-Groups-2016.pdf



FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

Functional groups are the characteristic groups in organic molecules that give them their reactivity. In the formulae below, R represents the rest of the molecule and X represents any halogen atom.

● Hydrocarbons ● Halogen-containing groups ● Oxygen-containing groups ● Nitrogen-containing groups ● Sulfur-containing groups ● Phosphorus-containing groups

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Figure 10.2.1: Functional groups in organic chemistry. (CC BY-NC-ND, CompoundChem.com).

10.3: The Structure of Organic Molecules - Alkanes and Their Isomers

Learning Objectives

- To identify simple alkanes as straight-chain or branched-chain.
- Describe and recognize structural and functional group isomers.

As you just learned, there is a wide variety of organic compounds containing different functional groups. However, all organic compounds are hydrocarbons, they contain hydrogen and carbon. The general rule for hydrocarbons is that any carbon must be bonded to at least one other carbon atom, except in the case of methane which only contains one carbon. The bonded carbons form the *backbone* of the molecule to which the hydrogen atoms (or other functional groups) are attached.

Hydrocarbons with only carbon-to-carbon single bonds (C–C) 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 these molecules.

> Saturated fats and oils are organic molecules that do not have carbon-to-carbon double bonds (C=C).

The three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) shown in Figure $10.3.1$, 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 (called methylene). Alkanes follow the general formula: 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 $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

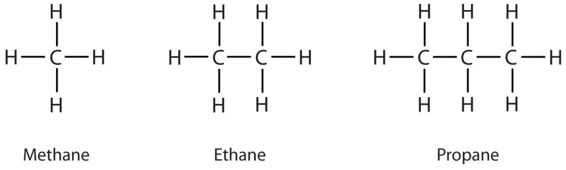
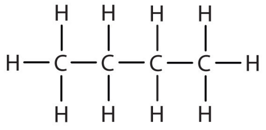


Figure 10.3.1: The Three Simplest Alkanes

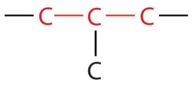
Isomers

Alkanes that contain one continuous chain of linked carbons are called **straight-chain** alkanes. As the number of carbons in a chain increases beyond three, the arrangement of atoms can expand to include **branched-chain** alkanes. In a branched chain, one or more hydrogen atoms along the chain is replaced by a carbon atom (or a separate chain of carbon atoms). It is important to note that while the structural arrangement of these chains are different, continuous versus branched, they both still follow the same general formula for alkanes as introduced above, C_nH_{2n+2}. In fact, alkane chains that have the same molecular formula (same number of carbon and hydrogen), but a different arrangement of atoms, are called **isomers**. Let's look at an example below:

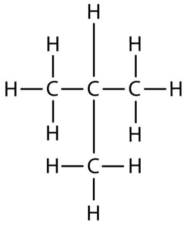
The structure of butane (C_4H_{10}) is written by stringing four carbon atoms in a row, and then adding enough hydrogen atoms to give each carbon atom four bonds:



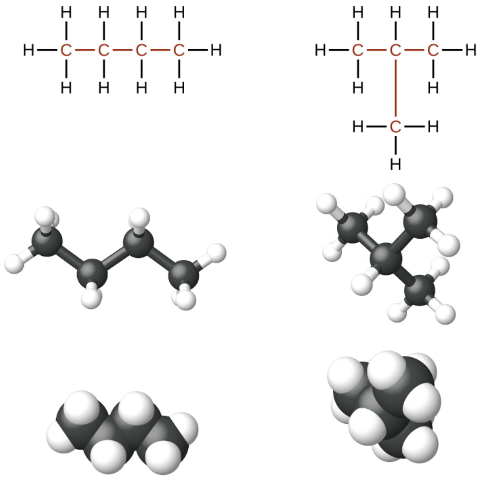
Butane is a straight-chain alkane, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then *branch* the fourth carbon off the middle carbon atom:



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



The result is the isomer 2-methylpropane (also called isobutane), which is a branched-chain alkane with the same formula as butane, (C_4H_{10}). However, it is a *different* molecule with a *different* name and *different* chemical properties. A side-by-side comparison of these two molecules is shown in the below figure.



n-butane

2-methylpropane

Figure 10.3.1: n-butane and 2-methylpropane. The compounds *n*-butane and 2-methylpropane are structural isomers, meaning they have the same molecular formula, C_4H_{10}, but different spatial arrangements of the atoms in their molecules. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching.

The four-carbon straight chain butane may be drawn with different bends or kinks in the backbone (Figure 10.3.2) because the groups can rotate freely about the C–C bonds. This rotation or bending of the carbon chain does *not* change the identity of the compound; all of the following structures represent the *same* compound, butane, with different bends in the chain:

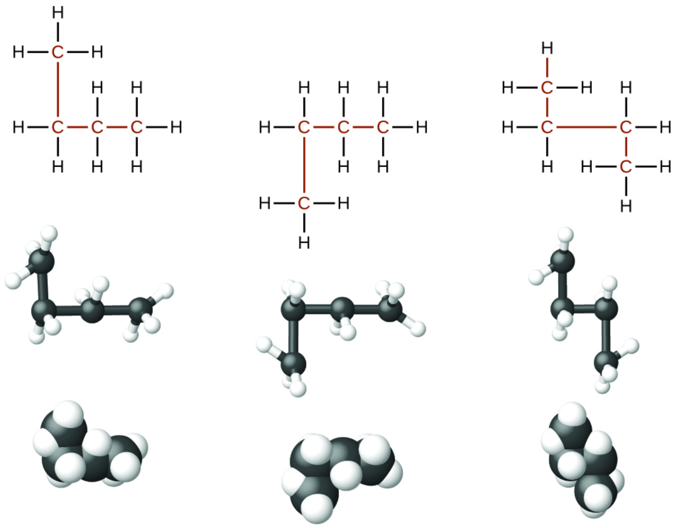
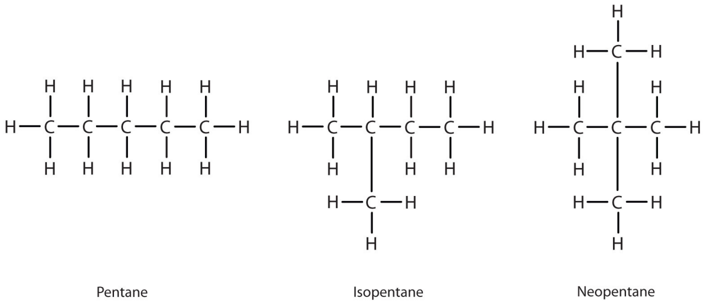


Figure 10.3.2: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

When identifying isomers, it is useful to trace the carbon backbone with your finger or a pencil and count carbons until you need to lift your hand or pencil to get the another carbon. Try this with each of the above arrangements of four carbons, then do the same with 2-methylpropane. Butane has a continuous chain of four carbons no matter how the bonds are rotated – you can connect the carbons in a line without lifting your finger from the page. How many continuous carbons are in the 2-methylpropane backbone? You should be able to count a continuous chain of three carbon atoms only, with the fourth carbon attached as a branch, (compare the two structures in Figure 10.3.1). In a later chapter, you will learn how to systematically name compounds by counting the number of carbons in the longest continuous chain and identifying any functional groups present.

Adding one more carbon to the butane chain gives pentane, which has the formula, C_5H_{12}. Pentane and its two branched-chain isomers are shown below. 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. The names isopentane and neopentane are common names for these molecules. As mentioned above, we will learn the systematic rules for naming compounds in later chapters.



> 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.

10.4: Drawing Organic Structures

Learning Objectives

- Draw condensed structures and line structures for simple compounds from the given molecular formulas.
- Convert between expanded, condensed and line structures.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the number and type 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 2-methylpropane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them (**expanded structure**). This type of structure allows for easy identification of specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas that show the bonds between *all* atoms are sometimes difficult to type/write and take up a lot of space, especially when the number of atoms greatly increases. Chemists often use **condensed structures**, that show hydrogen atoms right next to the carbon atoms to which they are attached, to alleviate these problems. The ultimate condensed formula is a **line (or line-angle) structure**, in which carbon atoms are implied at the corners and ends of lines rather than written out, and each carbon atom is understood to be attached to the appropriate amount of hydrogen atoms to give each carbon atom four bonds. Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom. All three of these structure types are illustrated for butane and its isomer, 2-methylpropane in Figure 10.4.1 below.

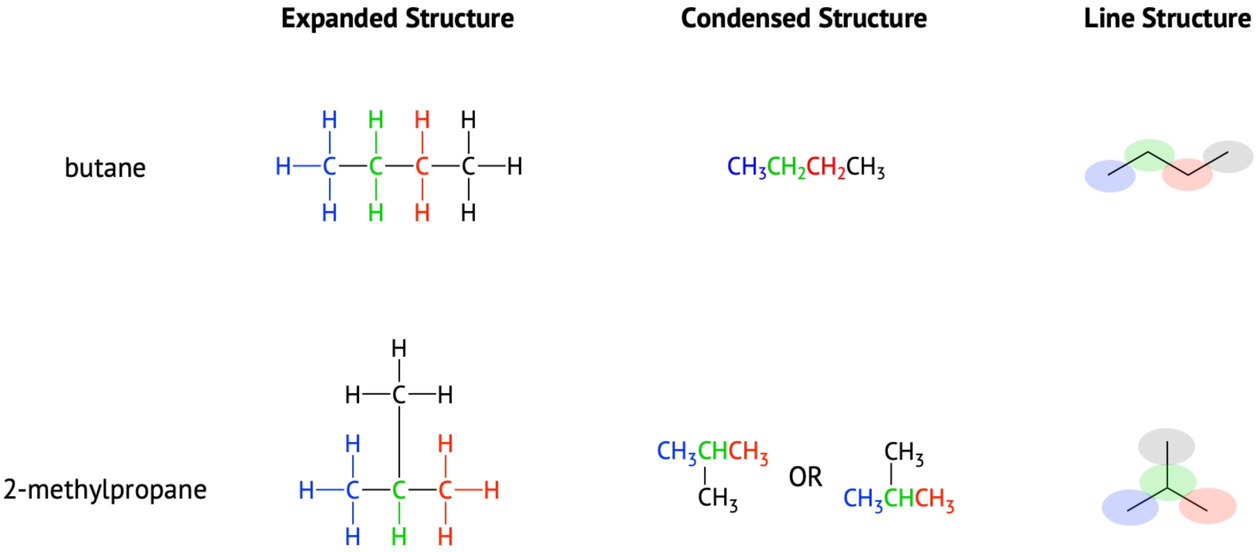


Figure 10.4.1: Structural representations for butane and its isomer, 2-methylpropane. (The colors are used to help identify carbons and do not represent any special properties.)

10.5: Naming Alkanes

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, etc. It would be difficult to assign each compound unique individual names that we could remember easily. 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 mentioned earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.)

In the IUPAC system, a compound is named according to the number of carbons in the longest continuous chain (LCC) or parent chain and the family it belongs to. Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by a numerical prefix at the beginning of the name:

Prefix (substituent) – Parent (# carbons) – Suffix (family name)

2-methylpropane

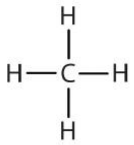
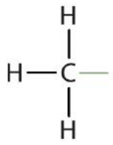
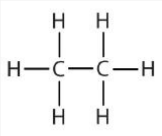
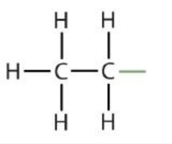
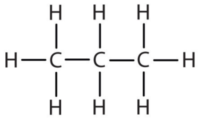
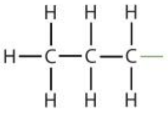
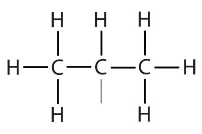
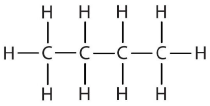
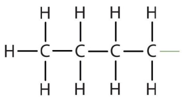
(Table 10.5.1) below lists the IUPAC parent names that are used for charbon chains containing 1 to 10 carbons, along with straight-chain alkane examples for each. Notice that the suffix for each example in this table is *-ane*, which indicates these are members of the alk*ane* family.

Table 10.5.1: Parent name for 1-10 carbons and Example Alkanes

Number of Carbons	Parent Chain (LCC) Name	Example Alkane Name	Example Condensed Structural Formula
1	*meth-*	methane	CH_4
2	*eth-*	ethane	CH_3CH_3
3	*prop-*	propane	$CH_3CH_2CH_3$
4	*but-*	butane	$CH_3CH_2CH_2CH_3$
5	*pent-*	pentane	$CH_3CH_2CH_2CH_2CH_3$
6	*hex-*	hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	*hept-*	heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	*oct-*	octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	*non-*	nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	*dec-*	decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Atoms or groups of atoms that branch off the parent chain are called **substituents**. When the substituent is a carbon or group of carbons, such as –CH_3 or –CH_2CH_3, it is called an **alkyl group**. Alkyl groups are alkanes that have had one hydrogen removed to allow for binding to a main chain carbon and are 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**. Removing a hydrogen from ethane, CH_3CH_3, gives –CH_2CH_3, or the **ethyl group**. The alkyl groups we will use most frequently are listed in Table 10.5.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 10.5.2: 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		$CH_3CH_2CH_2CH_2–$
		sec-butyl		
		isobutyl		
		tert-butyl (tBu)		

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 10.5.1).

Step 1: **Name the parent chain.** Find the longest continuous chain, (it may not always be the most obvious chain written in one line), and name according to the number of carbon atoms it contains. Add the suffix *-ane* to indicate that the molecule is an alkane. Use Table 10.5.1 as a reference to start, but it is a good idea to commit these to memory.

Step 2: **Number the carbon atoms in the parent chain,** giving carbons with any substituents attached the lowest number possible. These numbers are used to locate where substituents are attached to a main chain.

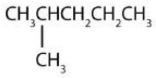
Step 3: **Name any substituents (including the location number).** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as 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.

Step 4: **Write the name of the compound as a single word placing the substituent groups first (in alphabetical order), then the parent name, then the family name.** Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other.

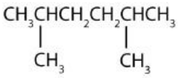
When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to practice it, not just memorize the rules. It’s easier than it looks.

Example 10.5.1

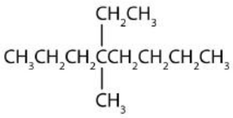
Name each compound.

1. 

$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CH_2CH_3$

- 

$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_3$

- 

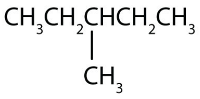
$CH_3CH_2CH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_2CH_3$

Solution

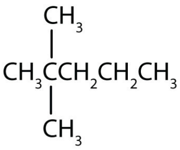
1. Step 1: The LCC has five carbon atoms, and so the parent compound name is pentane. Step 2: Number the carbons in the LCC from left to right. Step 3: There is a methyl group attached to carbon #2 of the pentane chain. Step 4: The name is 2-methylpentane.
2. Step 1: The LCC has six carbon atoms, so the parent compound is hexane. Step 2: Number the carbons in the LCC from left to right (or right to left, either way will be identical numbering). Step 3: There are two methyl groups attached to the second and fifth carbon atoms. Step 4: The name is 2,5-dimethylhexane.
3. Step 1: The LCC has eight carbon atoms, so the parent compound is octane. Step 2: Number the carbons in the LCC from left to right to give the *lower* number. Step 3: There are methyl and ethyl groups, both attached to the fourth carbon atom. Step 4: The correct name is thus 4-ethyl-4-methyloctane.

Exercise 10.5.1

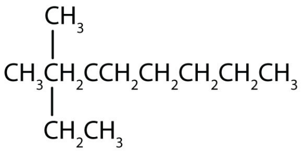
Name each compound.

1. 

$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CH_3$

- 

$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_3$

- 

$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}}CH_2CH_2CH_2CH_2CH_3$

Example 10.5.2

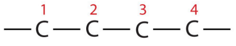
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

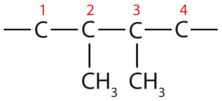
Solution

In drawing structures, always start with the parent chain.

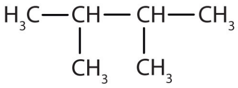
a. The parent chain is butane, indicating four carbon atoms in the LCC.



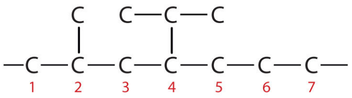
Then add the substituents at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (–CH_3) groups, one on the second carbon atom and one on the third.



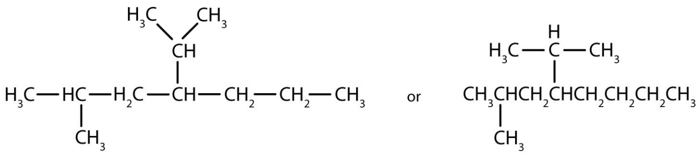
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds total.



- Adding the substituents at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas (both are correct):



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

? Exercise 10.5.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

10.6: 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 10.6.1 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 10.6.1: 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.

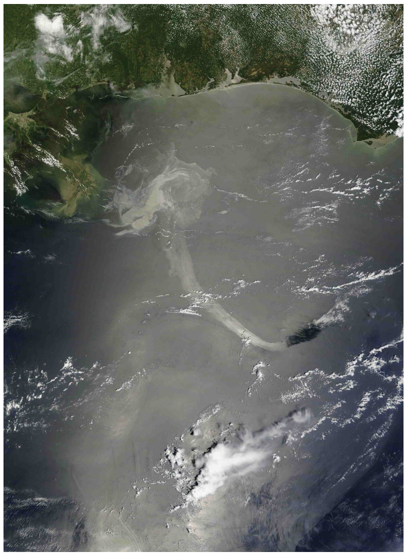


Figure 10.6.1: Oil Spills. Crude oil coats the water’s surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) 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 10.6.1 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 10.6.1 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.

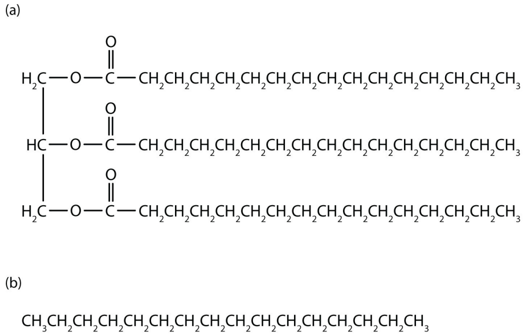


Figure 10.6.2: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

10.7: Reactions of Alkanes

Learning Objectives

- Understand the reactions of alkanes: combustion and halogenation.

Alkanes are relatively stable, nonpolar molecules, that will not react with acids, bases, or oxidizing or reducing reagents. Alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

However, heat or light can initiate the breaking of C–H or C–C single bonds in reactions called **combustion** and **halogenation**.

Combustion

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 **combustion** reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{10.7.1}$$

As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of straight- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure $10.7.1$). You may recall that boiling point is a function of intermolecular interactions, which was discussed in an earlier chapter.

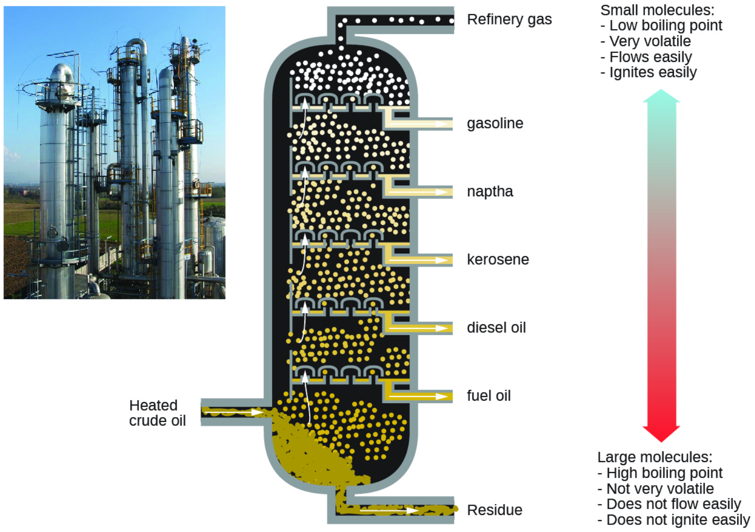


Figure 10.7.1:In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

If the reactants of combustion reactions are adequately mixed, and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and energy—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, other unwanted by-products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{10.7.2}$$

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.)

Halogenation

In **halogenation** reactions, alkanes 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).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{10.7.3}$$

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.

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 $10.7.1$, along with some of their uses.

Table 10.7.1: 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

Note 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.

Note 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 $10.7.2$

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.

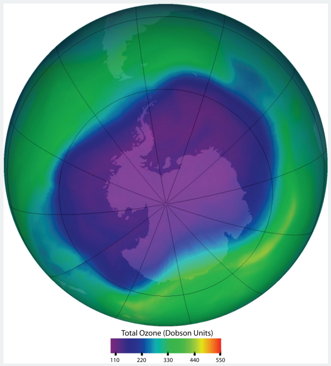


Figure $10.7.2$: Ozone in the upper atmosphere shields Earth’s surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone “holes” in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas 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, http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24.

- **12.7: Chemical Properties of Alkanes** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.
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10.8: Cycloalkanes

Learning Objectives

- Identify the structures of cycloalkanes.

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds and each carbon is bonded to two hydrogen atoms, they are saturated compounds. Cycloalkanes have the general formula C_nH_{2n}. The simplest of these cyclic hydrocarbons, cyclopropane, has the formula C_3H_6, which makes a three-carbon ring.

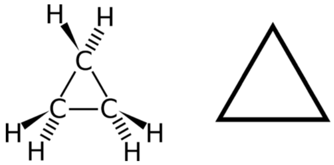
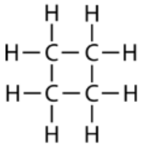


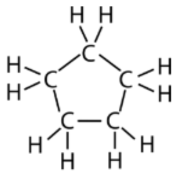
Figure 10.8.1: Cyclopropane is the simplest cycloalkane. Its highly strained geometry makes it rather unstable and highly reactive.

The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left from the figure above. A convenient shorthand is to omit the element symbols and only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes have a bond angle of 109.5^o. However, an examination of the cyclopropane structure shows that the triangular structure results in a $C-C-C$ bond angle of 60°. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane, with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108^o. This minimal ring strain for cyclopentane makes it a more stable compound.

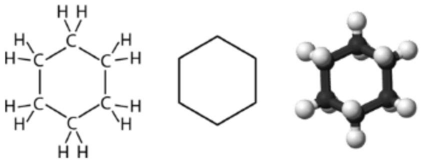


cyclobutane



cyclopentane

Cyclohexane is a six-carbon cycloalkane, shown below.



All three of the depictions of cyclohexane above are somewhat misleading, because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5^o, the molecule is actually puckered.

The ring structure in cycloalkanes also prevents rotation around the carbon–carbon bonds without breaking open the ring, thus they are more rigid and less flexible than acyclic alkanes. This property is called **restricted rotation**.

Note 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.

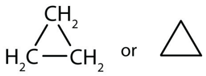
- **12.9: Cycloalkanes** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.
- **25.6: Cyclic Hydrocarbons** by CK-12 Foundation is licensed CK-12. Original source: https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/.

10.9: Drawing and Naming Cycloalkanes

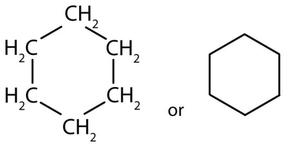
Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

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.



cyclopropane



cyclohexane

Some cyclic compounds have substituent groups attached. Example 10.9.1 interprets the name of a cycloalkane with a single substituent group.

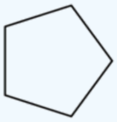
Example 10.9.1

Draw the structure for each compound.

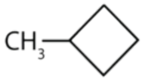
a. cyclopentane
b. methylcyclobutane

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 10.9.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane

CHAPTER OVERVIEW

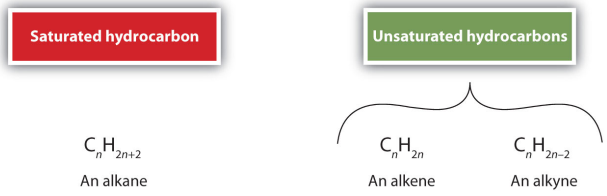
11: Unsaturated and Aromatic Hydrocarbons

11.1: Alkenes and Alkynes

Learning Objectives

- Identify the difference between saturated and unsaturated hydrocarbons.
- Describe the functional groups, alkenes and alkynes.

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 ($R{-}C{\equiv}C{-}R$). 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:



You have likely heard of *unsaturated fats*. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Alkenes

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 11.1.1); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

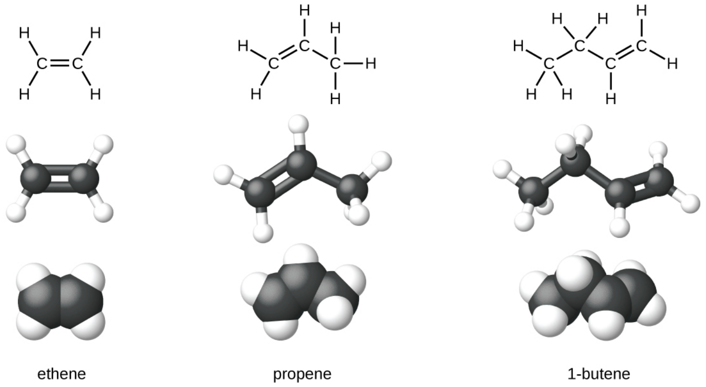


Figure 11.1.6: Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond have bond angles of 180°, giving these types of bonds a linear shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:

ethyne (acetylene)

> 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*.

11.2: The Structure of Alkenes- Cis-Trans Isomerism

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 11.2.1.

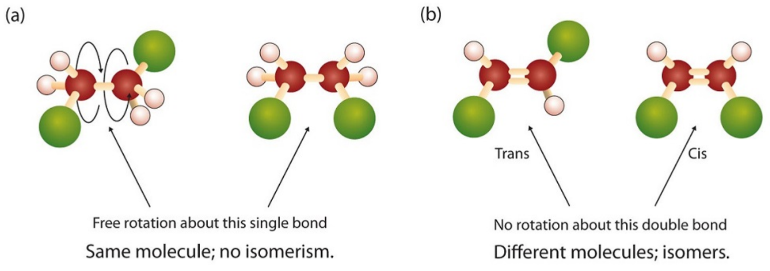
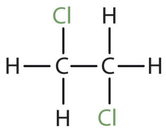
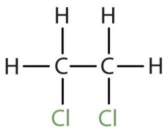


***Figure* 11.2.1** *: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure 11.2.1), 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 11.2.1b), 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 11.2.2).

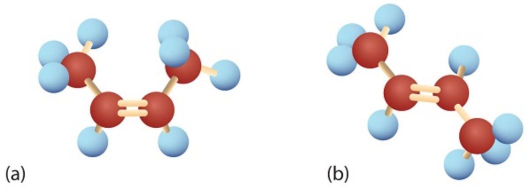


Figure 11.2.2: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

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 11.2.3**: 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 11.2.4). We can draw two *seemingly* different propenes:

***Figure 11.2.4**: 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 nomenclature 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 11.2.1

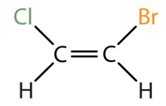
Which compounds can exist as cis-trans (geometric) isomers? Draw them.

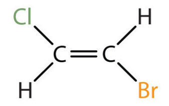
1. $CHCl{=}CHBr$
2. $CH_2{=}CBrCH_3$
3. $(CH_3)_2C{=}CHCH_2CH_3$
4. $CH_3CH{=}CHCH_2CH_3$

Solution

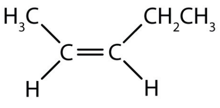
All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

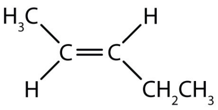
1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:





- 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.
- 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.
- This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:

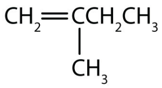




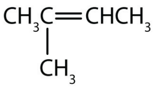
Exercise 11.2.1

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.



$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2CH_3$

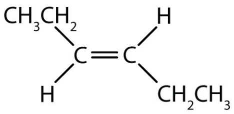
- 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3$

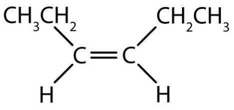
Concept Review Exercises

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.

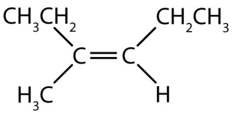
a.

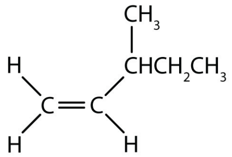


b.



c.



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 (fliping the bond does not change the molecule. There are no isomers for this molecule)

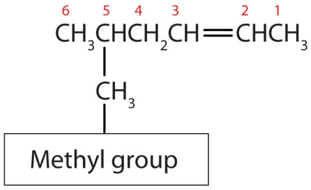
11.3: Naming Alkenes and Alkynes

Learning Objectives

- Understand and apply the IUPAC rules for naming alkenes
- Understand and apply the IUPAC rules for naming alkynes.

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.*

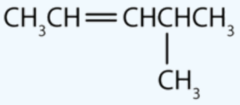


$$\overset{6}{CH_3}\underset{\substack{|\\ CH_3}}{\overset{5}{C}H}\overset{4}{CH_2}\overset{3}{CH}{=}\overset{2}{CH}\overset{1}{CH_3}$$

Example 11.3.1

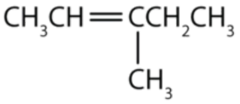
Name each compound.

a.



$$CH_3CH{=}CH\underset{\substack{|\\ CH_3}}{CH}CH_3$$

b.



$$CH_3CH{=}\underset{\substack{|\\ CH_3}}{C}CH_2CH_3$$

Solution

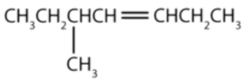
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 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 11.3.1

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

- 
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH{=}CHCH_2CH_3$

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.

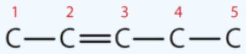
Example 11.3.2

Draw the structure for each compound.

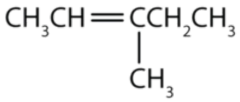
1. 3-methyl-2-pentene
2. cyclohexene

Solution

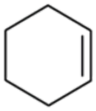
1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:


$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$

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.


$CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2CH_3$

- 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 11.3.2

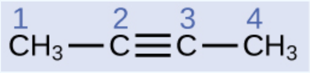
Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix -*yne* is used to indicate a triple bond in the chain. For example, $CH_3CH_2C\equiv CH$ is called 1-butyne.

Example 11.3.6: Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:

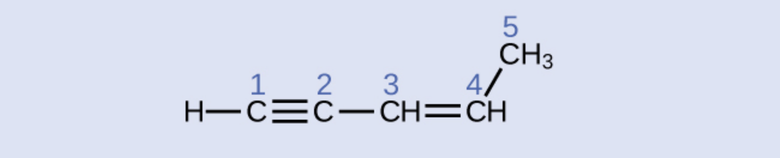

$\overset{1}{CH_3}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{CH_3}$

Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as *sp* hybrids.

? Exercise 11.3.6

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



Answer

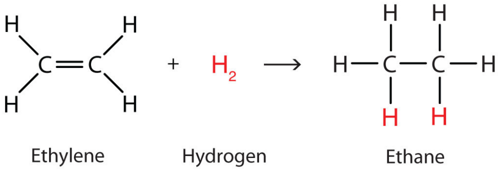
carbon 1: *sp*, 180°; carbon 2: *sp*, 180°; carbon 3: sp^2, 120°; carbon 4: sp^2, 120°; carbon 5: sp^3, 109.5°

11.4: Addition Reactions of Alkenes

Learning Objectives

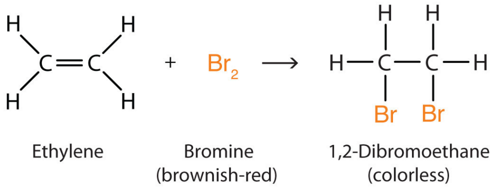
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

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).

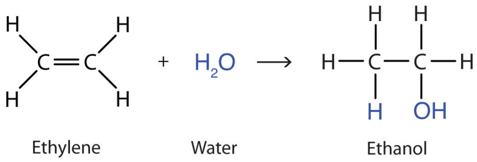


The product is an alkane having the same carbon skeleton as the alkene.

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.

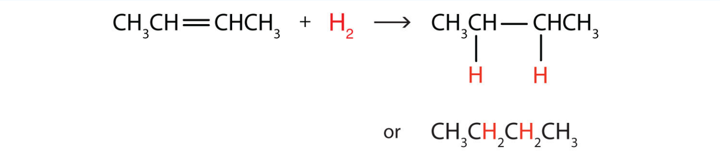
Example 11.4.1

Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

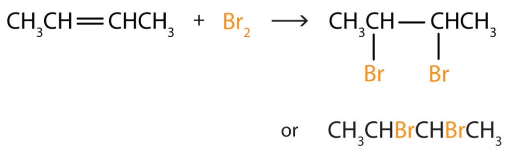
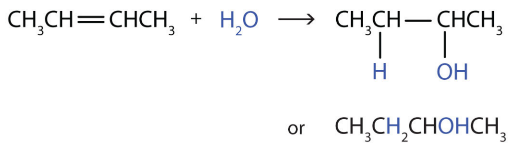
a. H_2 (Ni catalyst)
b. Br_2
c. H_2O (H_2SO_4 catalyst)

Solution

In each reaction, the reagent adds across the double bond.

a. 

$$CH_3CH{=}CHCH_3 + H_2 \longrightarrow CH_3\underset{H}{CH}-\underset{H}{CH}CH_3 \quad \text{or} \quad CH_3CH_2CH_2CH_3$$

- 
  $$CH_3CH{=}CHCH_3 + Br_2 \longrightarrow \underset{\displaystyle Br}{CH_3\overset{}{CH}}-\underset{\displaystyle Br}{CHCH_3}$$
  $$\text{or} \quad CH_3CHBrCHBrCH_3$$
- 
  $$CH_3CH{=}CHCH_3 + H_2O \longrightarrow \underset{\displaystyle H}{CH_3CH}-\underset{\displaystyle OH}{CHCH_3}$$
  $$\text{or} \quad CH_3CH_2CHOHCH_3$$

? Exercise 11.4.1

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)

11.5: Aromatic Compounds and the Structure of Benzene

Learning Objectives

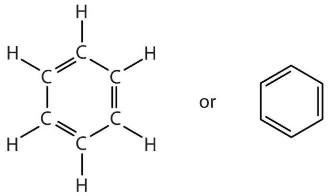
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

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.

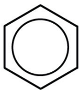
The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

> Note
>
> 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.

CHAPTER OVERVIEW

12: Organic Compounds of Oxygen and Nitrogen

Ethanol and resveratrol, a phenol, are representatives of two of the families of oxygen-containing compounds that we consider in this chapter. Two other classes, aldehydes and ketones, are formed by the oxidation of alcohols. Ethers, another class, are made by the dehydration of alcohols.

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12.1: Alcohols - Nomenclature and Classification

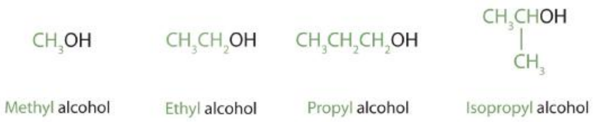
Learning Objectives

- 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 $12.1.1$ shows some examples of the application of these rules.

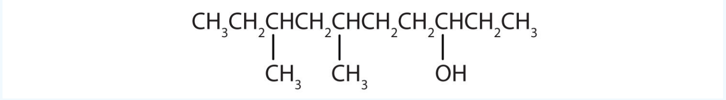
Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3

Figure 12.1.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Example 12.1.1

Give the IUPAC name for each compound.

a.



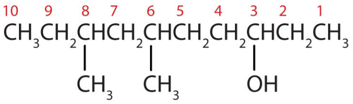
$$\underset{\displaystyle CH_3}{CH_3CH_2\overset{|}{C}HCH_2}\underset{\displaystyle CH_3}{\overset{|}{C}HCH_2CH_2}\underset{\displaystyle OH}{\overset{|}{C}HCH_2CH_3}$$

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

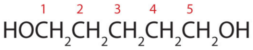
a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$

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).

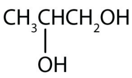
b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



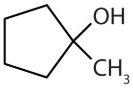
$HOCH_2CH_2CH_2CH_2CH_2OH$

Exercise 12.1.1

Give the IUPAC name for each compound.

a. 

$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$

- 

Example 12.1.2

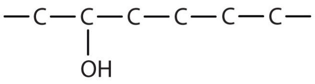
Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

Solution

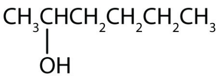
a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

The 2 indicates that the OH group is attached to the second carbon atom.



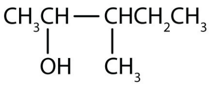
$—C—\underset{\displaystyle OH}{\underset{|}{C}}—C—C—C—C—$

Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2CH_2CH_3$

- 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.



$CH_3\underset{\displaystyle OH}{\underset{|}{C}}H—\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

Exercise 12.1.2

Draw the structure for each compound.

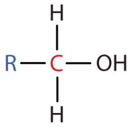
a. 3-heptanol

- 2-methyl-3-hexanol

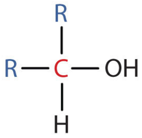
Classification of Alcohols

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.

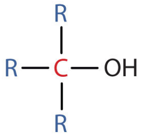
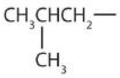
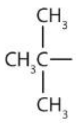


Table 12.1.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound’s classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Isobutyl group

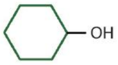
Sec-butyl group



Tert-butyl group

Table 12.1.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Summary

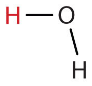
In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

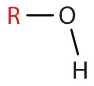
12.2: Physical Properties of Alcohols

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 12.2.1).

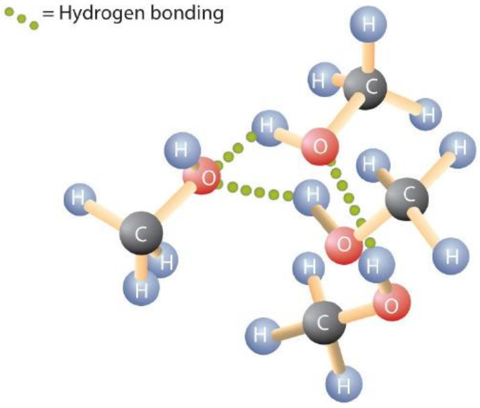


Figure 12.2.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 12.2.1 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 12.2.1: 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 12.2.2). 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.

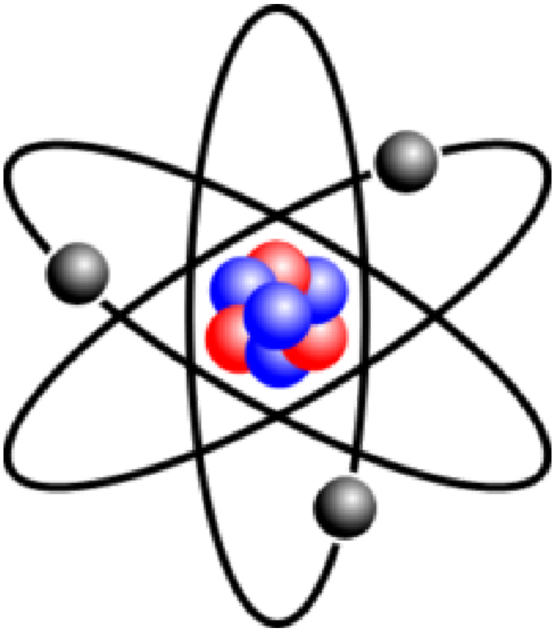


Figure 12.2.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

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.

12.3: Reactions that Form Alcohols

Learning Objectives

- To describe how to prepare alcohols from alkenes

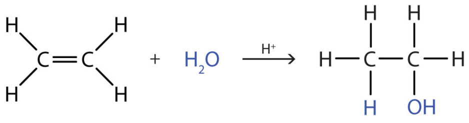
Methanol is prepared by combining hydrogen gas and carbon monoxide at high temperatures and pressures in the presence of a catalyst composed of zinc oxide (ZnO) and chromium oxide (Cr_2O_3) catalyst:

$$2H_2 + CO \xrightarrow[\text{ZnO, Cr}_2\text{O}_3]{200\text{ atm, }350^\circ\text{C}} CH_3OH$$

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.

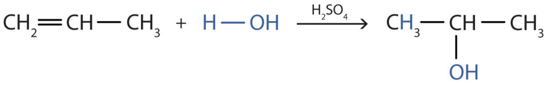
> *Nearly 2 billion gallons of methanol are produced each year in the United States by the catalytic reduction of carbon monoxide with hydrogen gas.*

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).



$$CH_2{=}CH{-}CH_3 + H{-}OH \xrightarrow{H_2SO_4} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

Propylene

Isopropyl alcohol
(2-propanol)

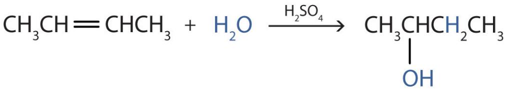
Additional Exercise 12.3.1 describes how to use a generalization called Markovnikov’s rule to predict the results when the addition of water to an alcohol has two possible products.

Example 12.3.1

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.



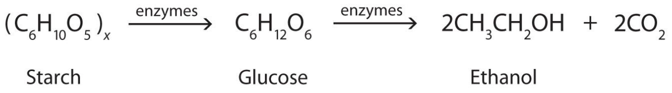
$$CH_3CH{=}CHCH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_2CH_3$$

Exercise 12.3.1

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.*
>
> $$^{-}OOCCH{=}CHCOO^{-} + HOH \xrightleftharpoons{\text{enzyme}} {}^{-}OOCCH_2CHOHCOO^{-}$$

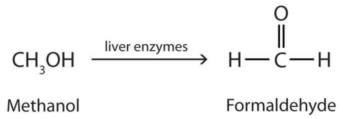
In addition to its preparation from ethylene, ethanol is made by the fermentation of sugars or starch from various sources (potatoes, corn, wheat, rice, etc.). Fermentation is catalyzed by enzymes found in yeast and proceeds by an elaborate multistep mechanism. We can represent the overall process as follows:



$$(C_6H_{10}O_5)_x \xrightarrow{\text{enzymes}} C_6H_{12}O_6 \xrightarrow{\text{enzymes}} 2CH_3CH_2OH + 2CO_2$$

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:

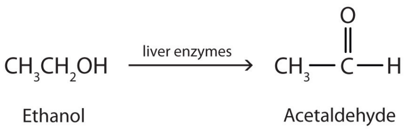


$$CH_3OH \xrightarrow{\text{liver enzymes}} H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

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:



$$CH_3CH_2OH \xrightarrow{\text{liver enzymes}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

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.

12.4: 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 12.4.1, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

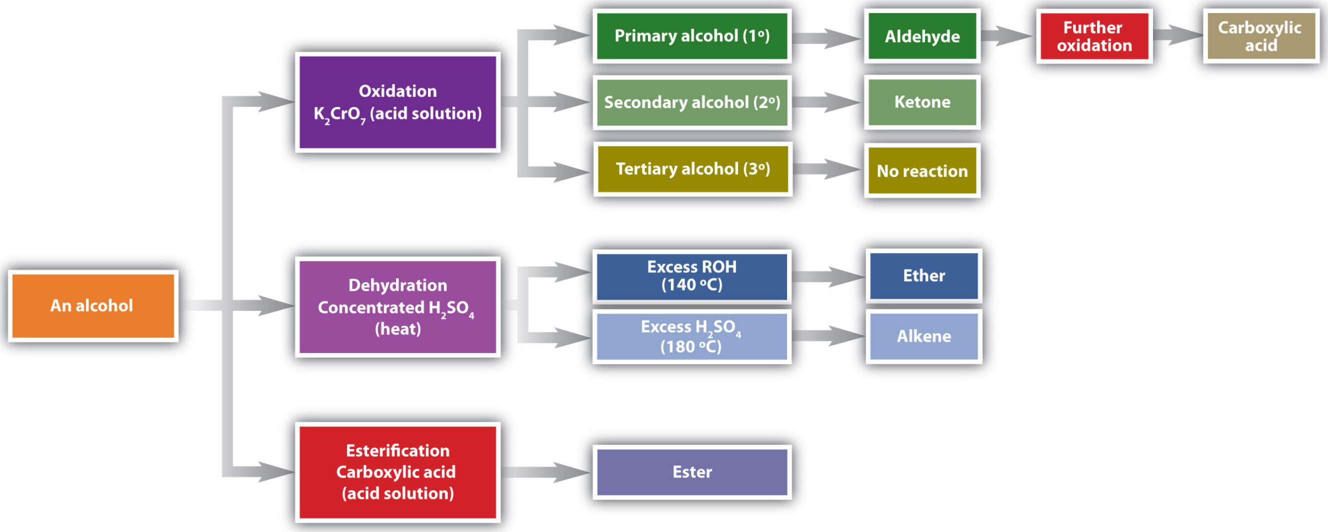
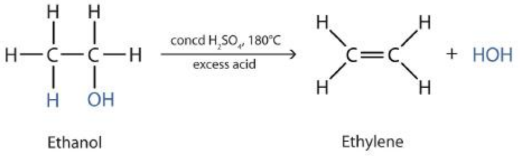


Figure 12.4.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

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.

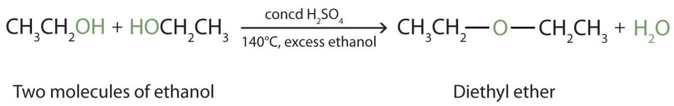
Dehydration

As noted in Figure 12.4.1, 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:



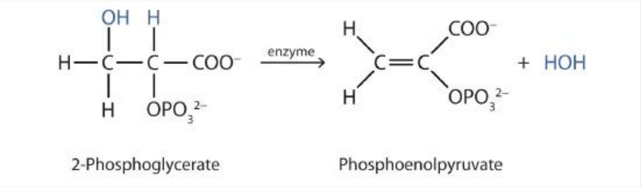
Structural formula of ethanol dehydrating under excess concentrated sulfuric acid at 180 degrees celsius. The products are ethylene and a side product of a water molecule.

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.

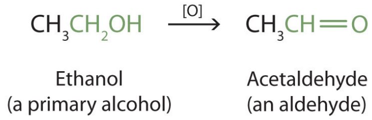
(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

> 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.

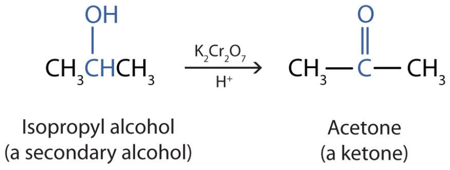
Oxidation

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.

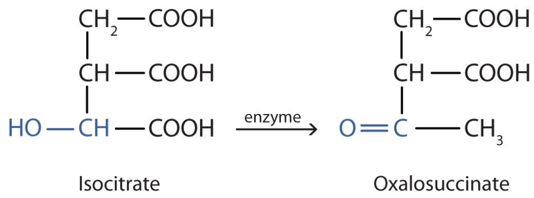
We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketones*. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:



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:



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 12.4.1

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.

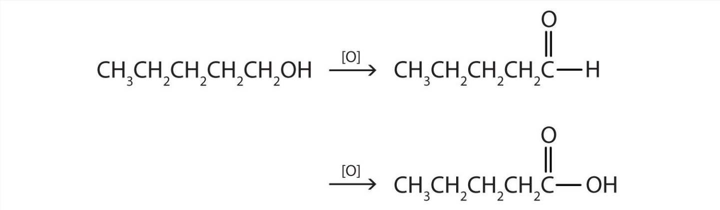
c. 

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

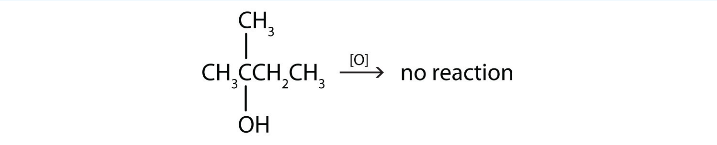
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

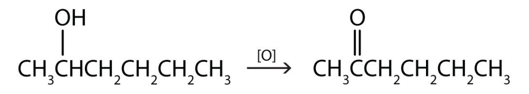
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



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.

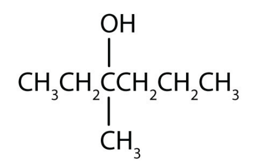


$$CH_3\overset{OH}{CH}CH_2CH_2CH_2CH_3 \xrightarrow{[O]} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$$

Exercise 12.4.1

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.

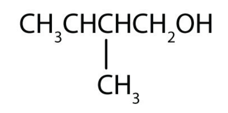
a.



$$CH_3CH_2\underset{CH_3}{\overset{OH}{C}}CH_2CH_2CH_3$$

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group and methyl group on carbon 3.

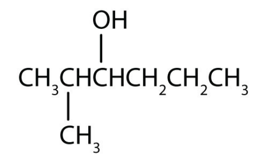
b.



$$CH_3CH\underset{CH_3}{CH}CH_2OH$$

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.



$$CH_3\underset{CH_3}{CH}\overset{OH}{CH}CH_2CH_2CH_3$$

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

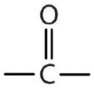
Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

12.5: Aldehydes and Ketones- Structure and Names

Learning Objectives

- Identify and describe a carbonyl functional group.
- Describe the general structure for an aldehyde and a ketone.
- Determine whether a compound is an aldehyde or a ketone based on a molecular structure and a name.

The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.

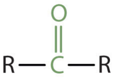


$$-\overset{O}{\overset{\|}{C}}-$$

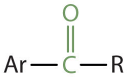
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *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.*

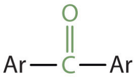
In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.



$$R-\overset{O}{\overset{\|}{C}}-R$$

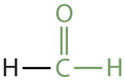


$$Ar-\overset{O}{\overset{\|}{C}}-R$$

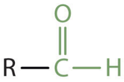


$$Ar-\overset{O}{\overset{\|}{C}}-Ar$$

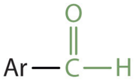
In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:



$$H-\overset{O}{\overset{\|}{C}}-H$$



$$R-\overset{O}{\overset{\|}{C}}-H$$



$$Ar-\overset{O}{\overset{\|}{C}}-H$$

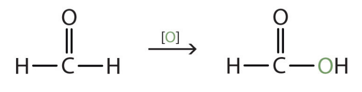
In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O).

—CHO	—CO—
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.

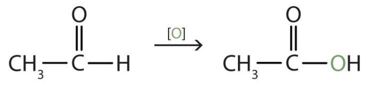
Naming Aldehydes and Ketones

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*.



$$\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}H \xrightarrow{[O]} H{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

Formaldehyde Formic acid



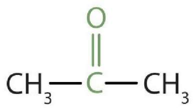
$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}H \xrightarrow{[O]} CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

Acetaldehyde Acetic acid

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-*

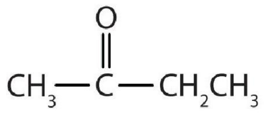
Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$$

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.

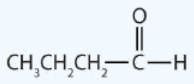


$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_3}$$

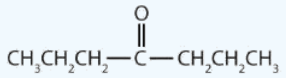
Ethyl methyl ketone

Example 12.5.1

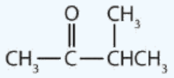
Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

a. 

$$\mathrm{CH_3CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}H}$$

b. 

$$\mathrm{CH_3CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_2CH_3}$$

c. 

$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}HCH_3}$$

Solution

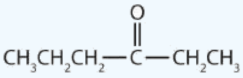
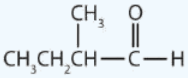
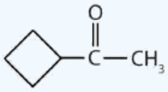
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

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 12.5.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

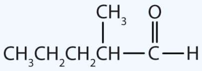
1. 
   $CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$
2. 
   $CH_3CH_2\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$
3. 

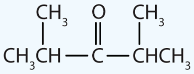
Here are some simple IUPAC rules for naming aldehydes and ketones:

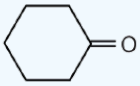
- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, 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 12.5.2

Give the IUPAC name for each compound.

a. 
$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$

b. 
$CH_3\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}HCH_3$

c. 

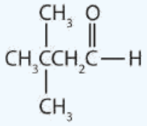
Solution

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

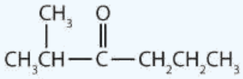
Give the IUPAC name for each compound.

a.



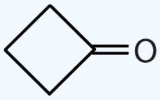
$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2\overset{O}{\overset{\|}{C}}{-}H$

b.



$CH_3\overset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2CH_3$

c.



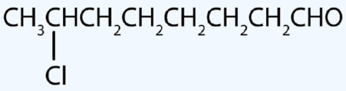
Example 12.5.3

Draw the structure for each compound.

a. 7-chlorooctanal
b. 4-methyl–3-hexanone

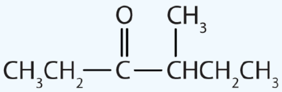
Solution

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.



$CH_3\underset{Cl}{CH}CH_2CH_2CH_2CH_2CH_2CHO$

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:



$CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{CH}CH_2CH_3$

Exercise 12.5.3

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

Summary

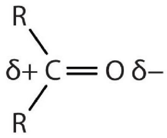
The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

12.6: 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 12.6.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

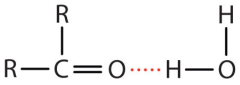
Table 12.6.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

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.

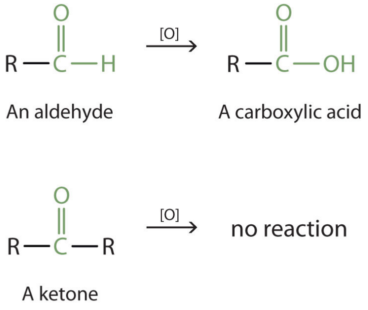
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.



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 12.6.1). Ordinary ketones do not react with Tollens' reagent.

Figure 12.6.1: 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 12.6.2).

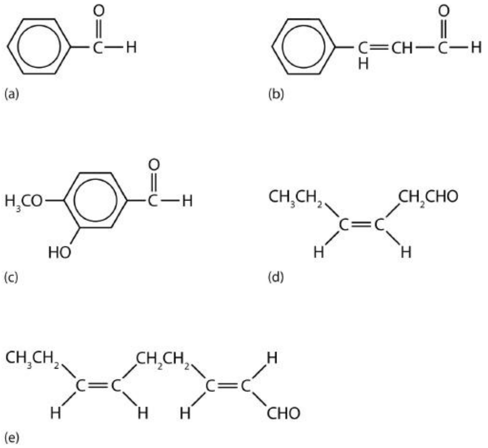


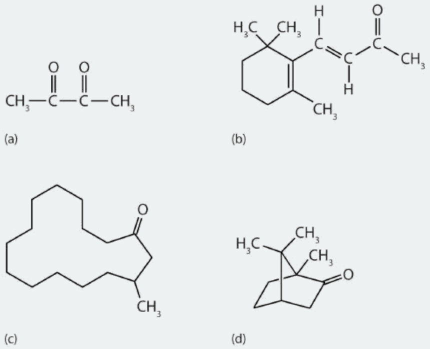
Figure 12.6.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

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.

12.7: Ethers

Learning Objectives

- Describe the general structure of an ether.
- Determine whether an organic compound is an ether from a molecular structure and a name.

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:

$$\text{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \text{ROR}' \xleftarrow[\text{of OH group}]{\text{replace H atom}} \text{ROH}$$

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 12.7.1).

Table 12.7.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

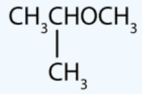
Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	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 12.7.1

What is the common name for each ether?

a. $CH_3CH_2CH_2OCH_2CH_2CH_3$

b. 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_3$

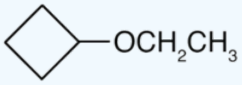
Solution

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 12.7.1

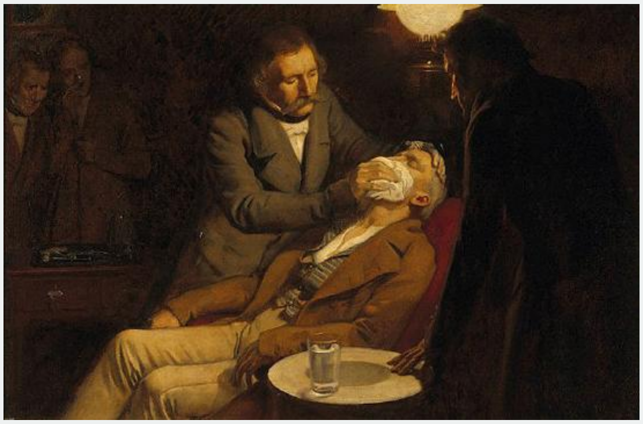
What is the common name for each ether?

a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$

b. 

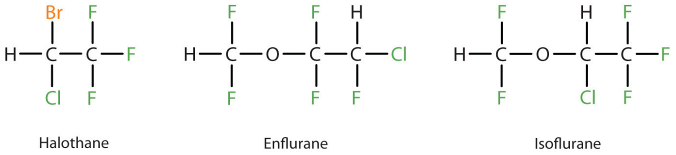
To Your Health: Ethers as General Anesthetics

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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12.8: Carboxylic Acids - Structures and Names

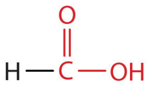
Learning Objectives

- Describe the general functional group of a carboxylic acid.
- Determine whether a compound is a carboxylic acid from a molecular structure and a name.

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 12.8.1). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.

Figure 12.8.1: 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

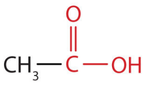
The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



$$H-\overset{\overset{\Large O}{\|}}{C}-OH$$

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.



$$CH_3-\overset{\overset{\Large O}{\|}}{C}-OH$$

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 $12.8.2$

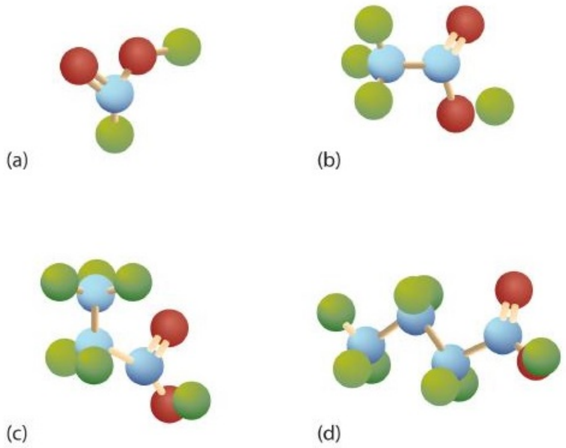
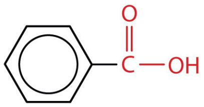


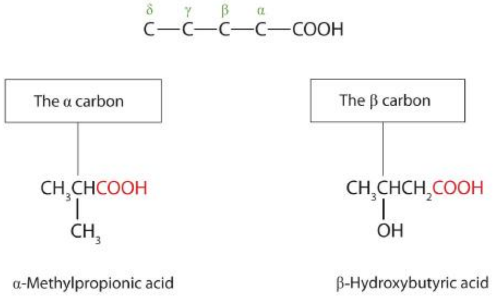
Figure $12.8.2$: Ball-and-Stick Models of Carboxylic Acids. Carboxylic acids feature a carbon atom doubly bonded to an oxygen atom and also joined to an OH group. The four acids illustrated here are formic acid (a), acetic acid (b), propionic acid (c), and butyric acid (d).

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 12.8.1

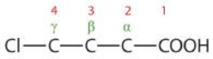
Give the common and IUPAC names for each compound.

1. $ClCH_2CH_2CH_2COOH$
2. 

$CH_3CH_2CHCOOH$ with Br on the CH

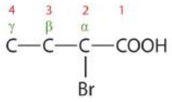
Solution

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 12.8.1

Give the IUPAC name for each compound.

a. $ClCH_2CH_2CH_2CH_2COOH$
b. $(CH_3)_2CHCH_2CHBrCOOH$

Example 12.8.2

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 12.8.2

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*.

12.9: Acidity of Carboxylic Acids

Learning Objectives

- Identify the acidic H atom in carboxylic acids.
- Write ionization reactions for carboxylic acids
- Describe the reactions between carboxylic acids and strong bases.

Ionization of Carboxylic Acids

Carboxylic acids are named such because they tend to be more acidic than other functional groups in organic chemistry. In dilute aqueous solutions, they act as *weak acids* that partially dissociate to produce the corresponding carboxylate anion and hydronium cation (H_3O^+). Carboxylate anions are named by replacing the *-ic acid* ending from the carboxylic acid with *-ate*, see examples below.

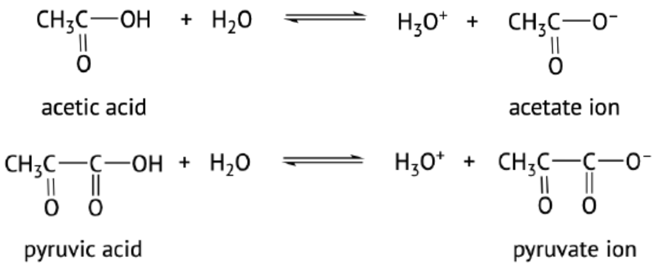


Table 12.9.1: Examples of Carboxylic Acid

Name	Compound
formic acid	$HCOOH$
acetic acid	CH_3COOH
propanoic acid	CH_3CH_2COOH
butanoic acid	$CH_3CH_2CH_2COOH$
chloroacetic acid	$ClCH_2COOH$
trichloroacetic acid	Cl_3CCOOH
hexanoic acid	$CH_3(CH_2)_4COOH$
benzoic acid	C_6H_5COOH
oxalic acid	$HOOCCOOH$
	$^-OOCCOOH$
glutaric acid	$HOOC(CH_2)_3COOH$
	$^-OOC(CH_2)_3COOH$

Neutralization of Carboxylic Acids

Carboxylic acids will react with bases such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) to form water and a **carboxylic acid salt**:

$$RCOOH + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O$$

$$2RCOOH + Na_2CO_3(aq) \rightarrow 2RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

$$RCOOH + NaHCO_3(aq) \rightarrow RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

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

Note

The salts of long-chain carboxylic acids are called soaps.

$CH_3(CH_2)_{13}CH_2COO^-Na^+$

Sodium palmitate (a soap)

Example 12.9.1

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 12.9.1

Write an equation for each reaction.

a. the ionization of formic acid in water
b. the ionization of *p*-chlorobenzoic acid in water

Example 12.9.2

Write an equation for the reaction of decanoic acid with each compound.

a. aqueous sodium hydoxide (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 12.9.3

Write an equation for the reaction of benzoic acid with each compound.

a. aqueous sodium hydroxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

Note 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.

$(CH_3CH_2COO^-)_2\,Ca^{2+}$

Calcium propionate

$CH_3CH{=}CHCH{=}CHCOO^-K^+$

Potassium sorbate

12.10: Esters - Structures and Names

Learning Objectives

- Describe the general structure for an ester.
- Determine whether a compound is an ester from a molecular structure and a name.

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 12.10.1shows models for two common esters.

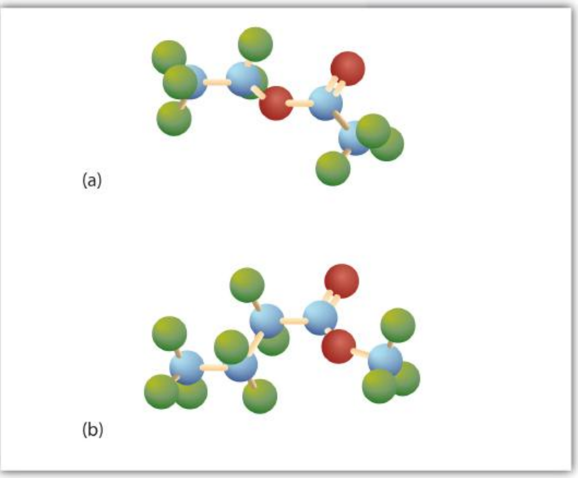


Figure 12.10.1: The Structure of Esters. Esters feature a carbon-to-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group. The esters shown here are ethyl acetate (a) and methyl butyrate (b).

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.

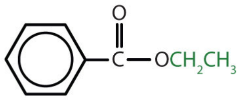
> Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

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 12.10.1).

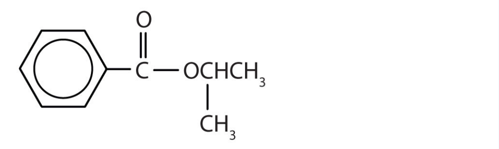
Table 12.10.1: Nomenclature of Esters

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

Condensed Structural Formula	Common Name	IUPAC Name
	ethyl benzoate	ethyl benzoate

✓ Example 12.10.1

Give the common and IUPAC names for each compound.

1. 
   $CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_3$
2. 

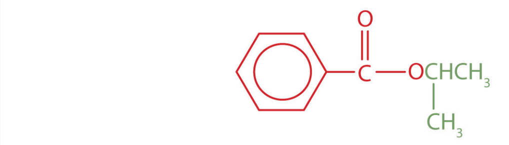
Solution

The alkyl group attached directly to the oxygen atom is a butyl group (in green).

$CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_3$

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.

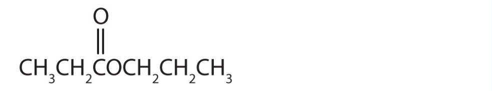
1. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).



? Exercise 12.10.1

Give the common and IUPAC names for each compound.

1. 
   $CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}—OCH_2CH_3$



$CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_3$

✓ Example 12.10.2

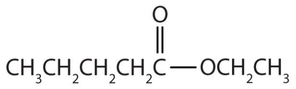
Draw the structure for ethyl pentanoate.

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.

$$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



$$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_3$$

? Exercise 12.10.2

Draw the structure for phenyl pentanoate.

Key Takeaway

- An ester has an OR group attached to the carbon atom of a carbonyl group.

12.11: Amines - Structures and Names

Learning Objectives

- Describe the general structure for an amine.
- Determine whether a compound is an amine from a molecular structure and a name.

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 12.11.1).

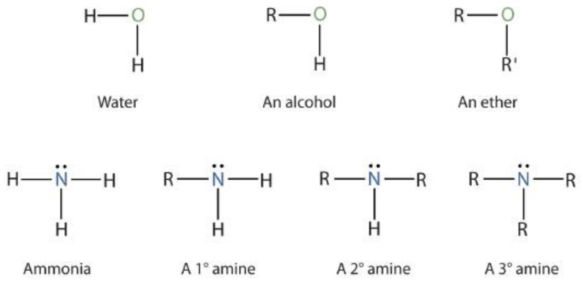


Figure 12.11.1: The Structure of Amines Compared to Water, an Alcohol, and an Ether

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.

$CH_3CH(NH_2)CH_3$

Isopropylamine
(a primary amine)

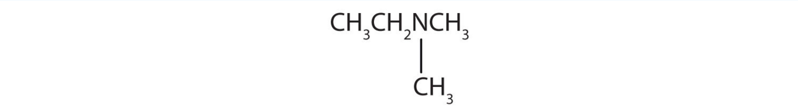
$CH_3CH(OH)CH_3$

Isopropyl alcohol
(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 12.11.1

Name and classify each compound.

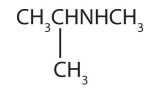
a. $CH_3CH_2CH_2NH_2$
b. 
$CH_3CH_2N(CH_3)CH_3$
c. $CH_3CH_2NHCH_2CH_3$
d. $CH_3CH_2CH_2NHCH_3$

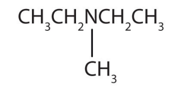
Solution

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 12.11.1

Name and classify each compound.

a. 
$CH_3\underset{\underset{CH_3}{|}}{C}HNHCH_3$

b. 
$CH_3CH_2\underset{\underset{CH_3}{|}}{N}CH_2CH_3$

c. $CH_3CH_2CH_2CH_2NH_2$

d. $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

Example 12.11.2

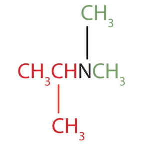
Draw the structure for each compound and classify.

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.


$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{N}CH_3$

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.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

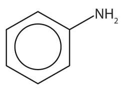
Exercise 12.11.2

Draw the structure for each compound and classify.

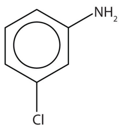
a. ethylisopropylamine

b. diethylpropylamine

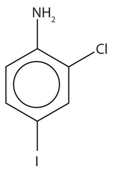
The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.



Aniline



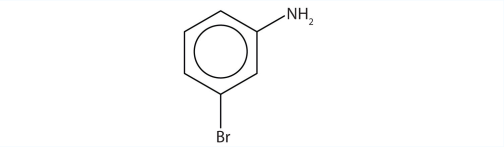
M-chloroaniline



2-Chloro-4-iodoaniline

Example 12.11.3

Name this compound.

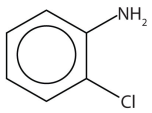


Solution

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 12.11.3

Name this compound.

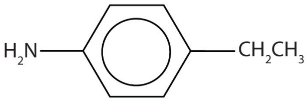


Example 12.11.4

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 12.11.4

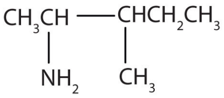
Draw the structure for *p*-isopropylaniline and classify.

Example 12.11.5

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.



$$\underset{\displaystyle NH_2}{\underset{|}{CH_3CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2CH_3$$

Exercise 12.11.5

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 12.11.6

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

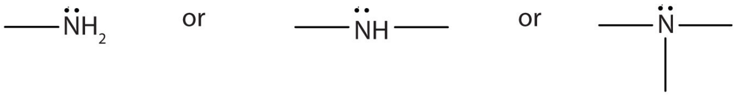
Exercise 12.11.6

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:



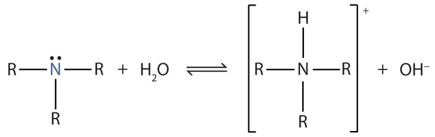
Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

12.12: Amines as Bases and Heterocylclic Amines

Learning Objectives

- Understand how an amine can act as a base.
- Write a reaction for an amine in water.
- Identify 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.

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Methylamine

Methylammonium ion

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$CH_3(CH_2)_6NH_2(l) + HNO_3(aq) \longrightarrow CH_3(CH_2)_6NH_3^+NO_3^-(aq)$$

Octylamine (insoluble)

Octylammonium nitrate (soluble)

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 $(CH_3CH_2CH_2)_3NH^+I^-$?

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

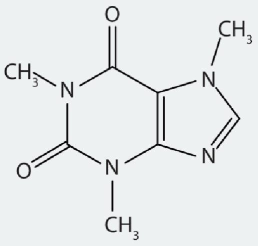
Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning “other”), nitrogen, oxygen, sulfur, or some other atom is incorporated 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.

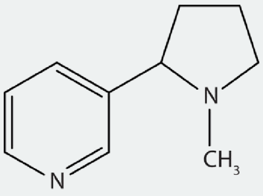
To Your Health: Three Well-Known Alkaloids

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.



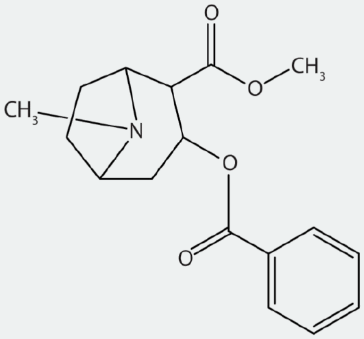
Caffeine

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

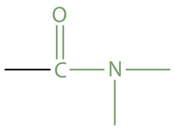
Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

12.13: Amides- Structures and Names

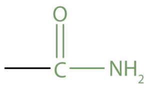
Learning Objectives

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Recognize amides from molecular structures and names.

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*.

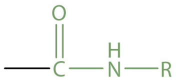


The amide group



$-\overset{\overset{O}{\|}}{C}-NH_2$

A simple amide

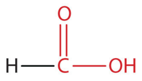


$-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-R$

A substituted amide

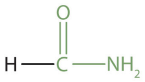
> The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

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*.



$H-\overset{\overset{O}{\|}}{C}-OH$

Formic acid
(methanoic acid)

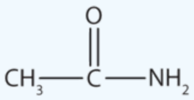


$H-\overset{\overset{O}{\|}}{C}-NH_2$

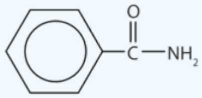
Formamide
(methanamide)

Example 12.13.1

Name each compound with the common name, the IUPAC name, or both.

a. 

$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

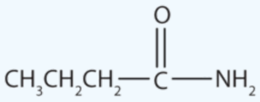
b. 

Solution

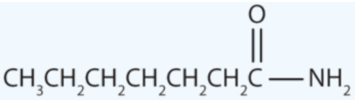
a. This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an NH_2 group. The -*ic* from *acetic* (or -*oic* from ethanoic) is dropped, and -*amide* is added to give *acetamide* (or ethanamide in the IUPAC system).
b. This amide is derived from benzoic 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. 

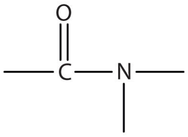
$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-NH_2$

b. 

$CH_3CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}{-}NH_2$

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*.

CHAPTER OVERVIEW

13: Carbohydrates

Glucose is one of the carbohydrates you will learn about in this chapter as we begin the study of biochemistry—the chemistry of molecules found in living organisms. Later we will study the other three major types of macromolecules found in living organisms: lipids, proteins, and nucleic acids.

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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.

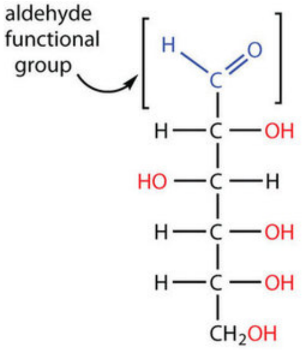
Figure 13.1.1: Using a Glucose Meter to Test Blood Glucose Level. (Public Domain; Centers for Disease Control and Prevention).

13.2: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

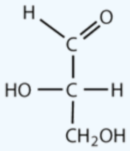
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. 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 $C_6{\cdot}6H_2O$.

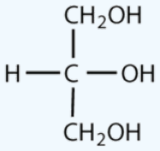


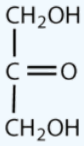
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

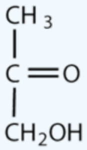
Example 13.2.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

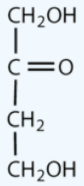
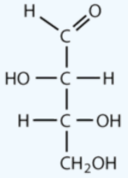
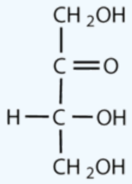
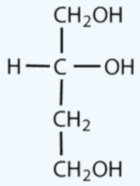
Solution

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

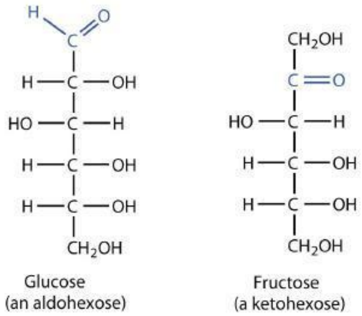
Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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.



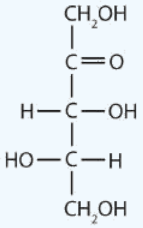
Example 13.3.1

Draw an example of each type of compound.

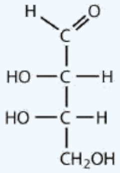
a. a ketopentose
b. an aldotetrose

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.

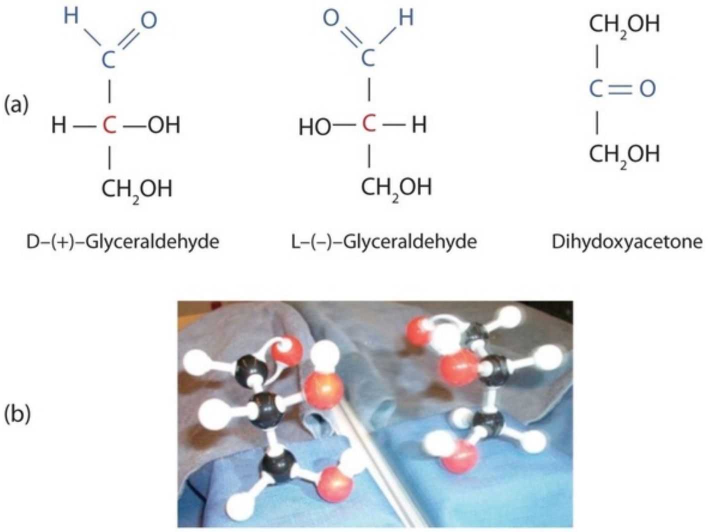


Figure 13.3.1: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

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°.

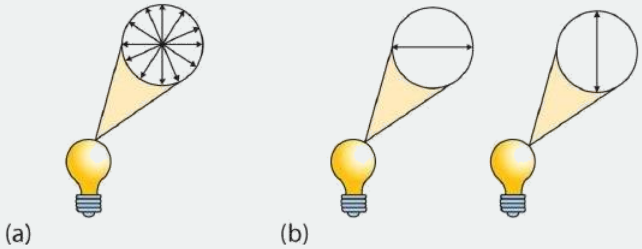
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure 13.3.1. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that are 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.

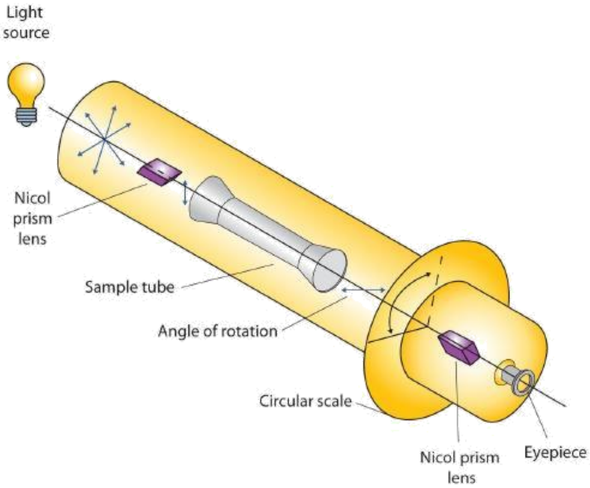


Figure 13.3.2: Diagram of a Polarimeter

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.

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.

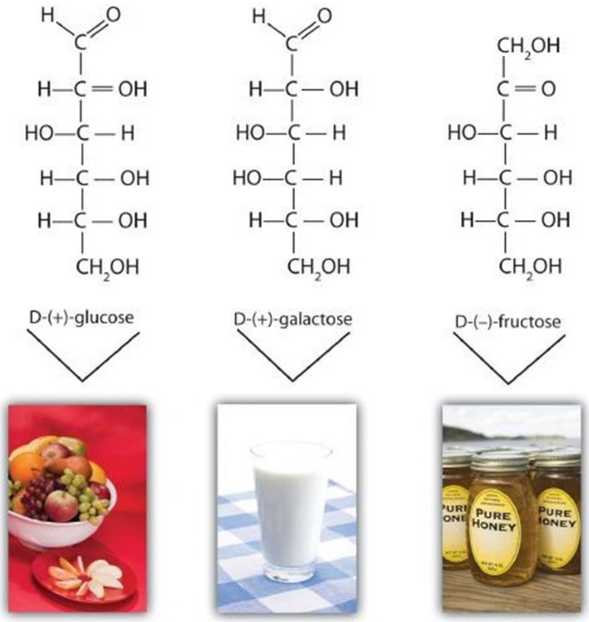


Figure 13.4.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

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.

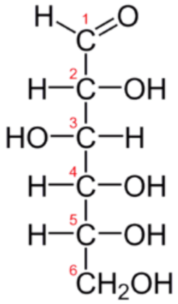


Figure 13.4.2: Fischer projection of D-glucose

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

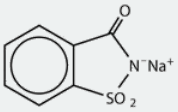
Looking Closer: Artificial Sweeteners

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.

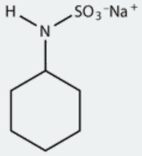
The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short 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

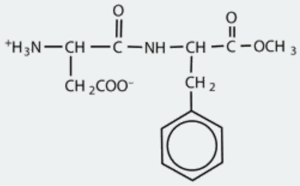
FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



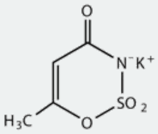
Saccharin



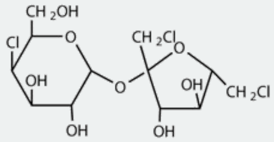
Cyclamate



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

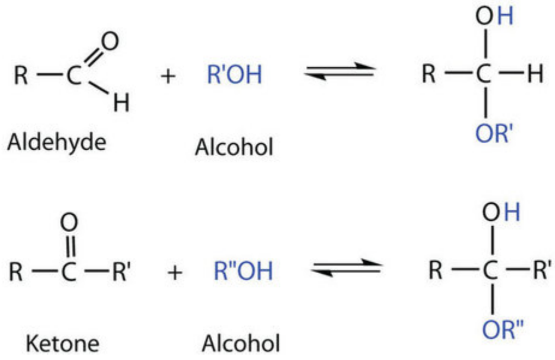
Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.

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.

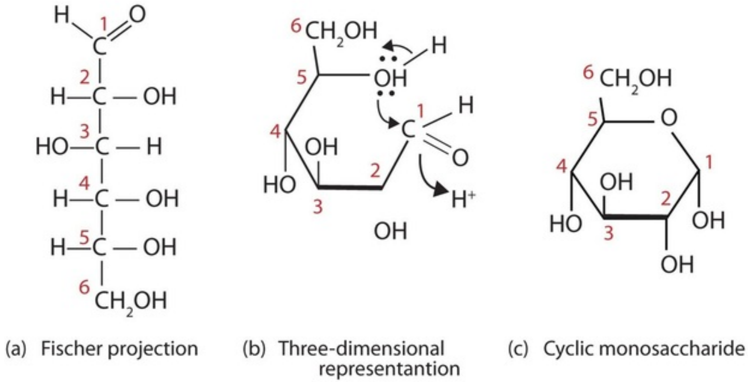


Figure 13.5.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

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°.

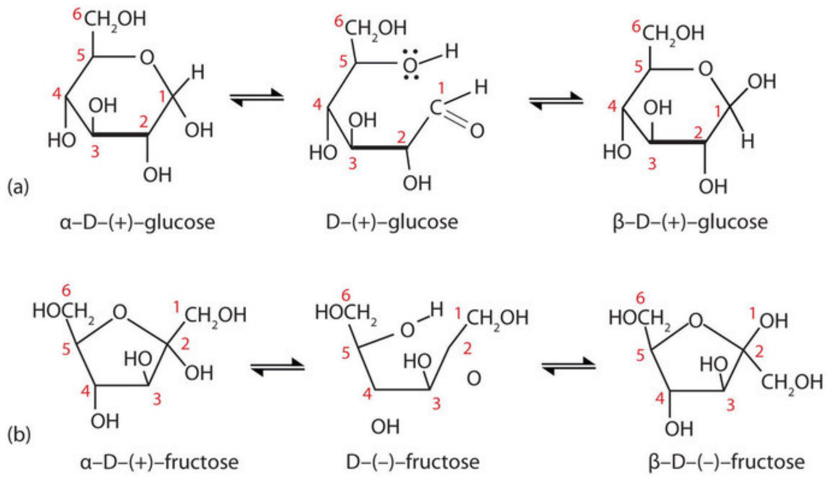


Figure 13.5.2: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

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.

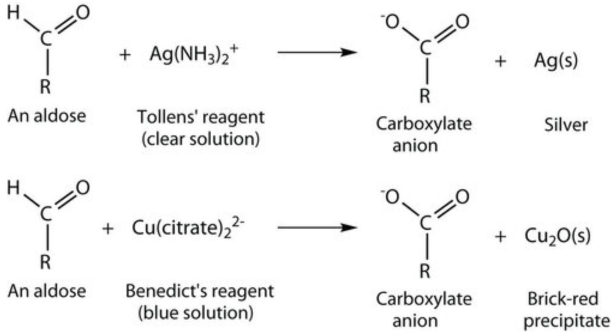
13.6: Properties of Monosaccharides

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*.

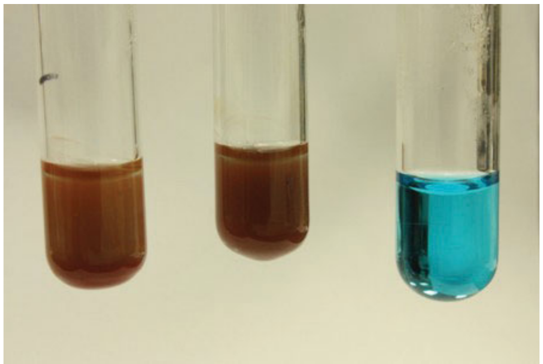


Figure 13.6.1: Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.

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

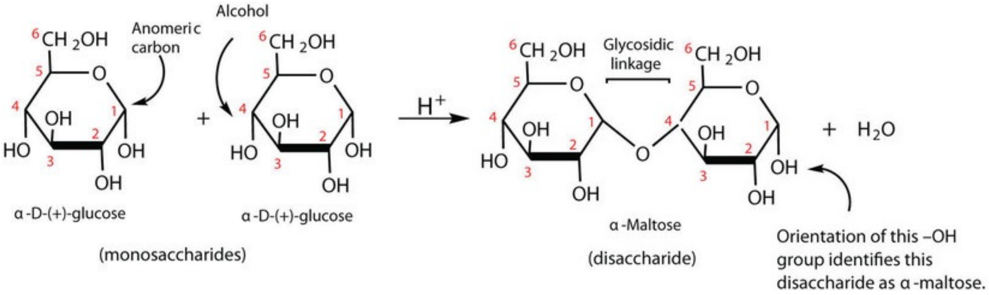
Monosaccharides are crystalline solids at room temperature and quite soluble in water. Monosaccharides are reducing sugars; they reduce mild oxidizing agents, such as Tollens' or Benedict's reagents.

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 $13.7.1$.

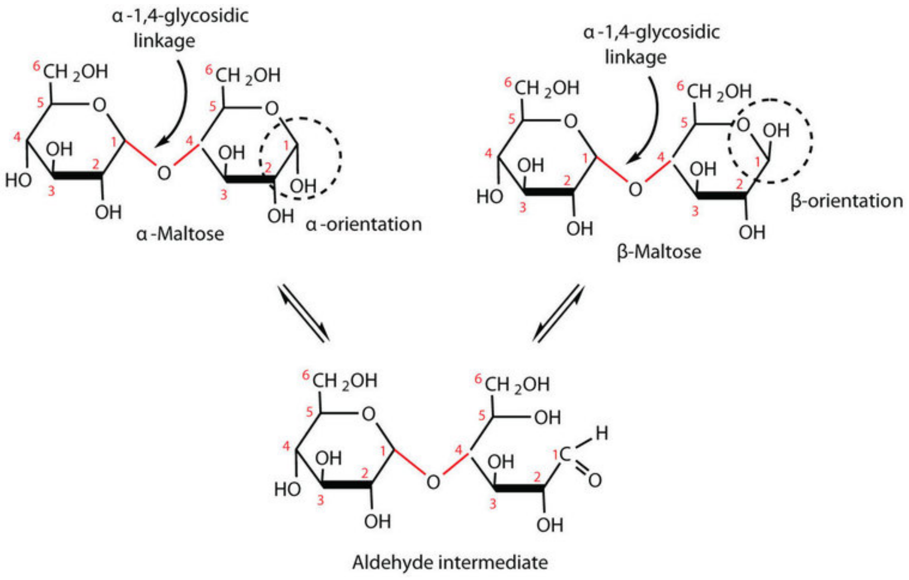
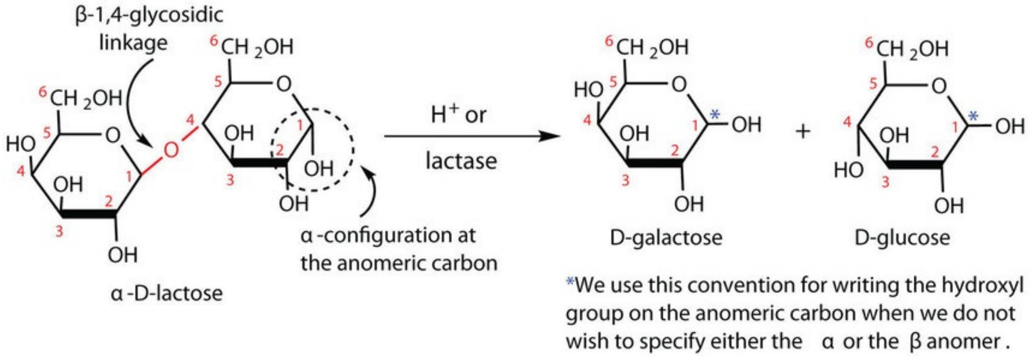


Figure 13.7.1: An Equilibrium Mixture of Maltose Isomers

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.

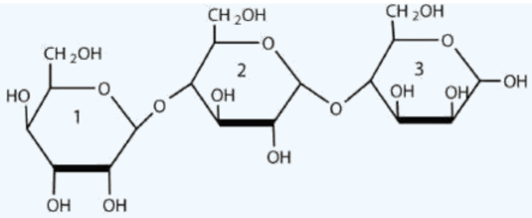
Lactose is a reducing sugar composed of one molecule of D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic 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.

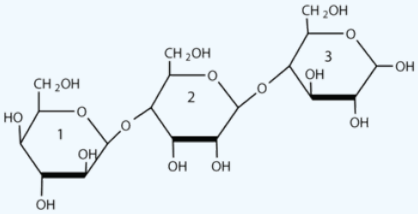


Solution

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.

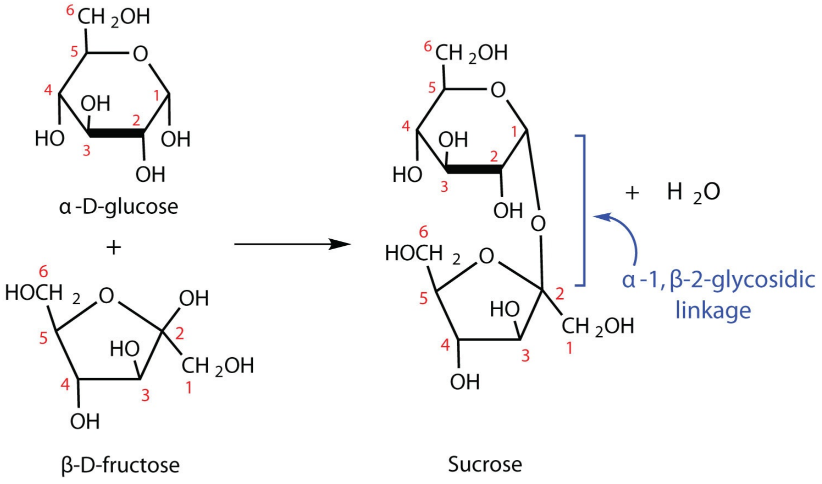
Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. 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

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.

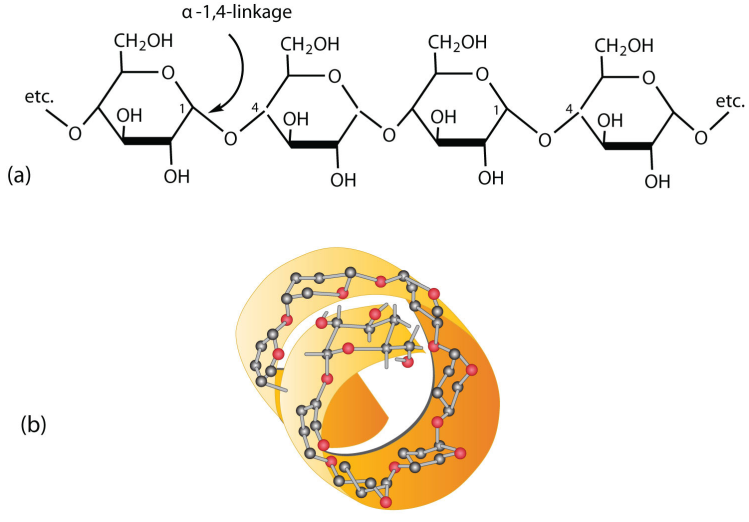


Figure 13.8.1: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

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.

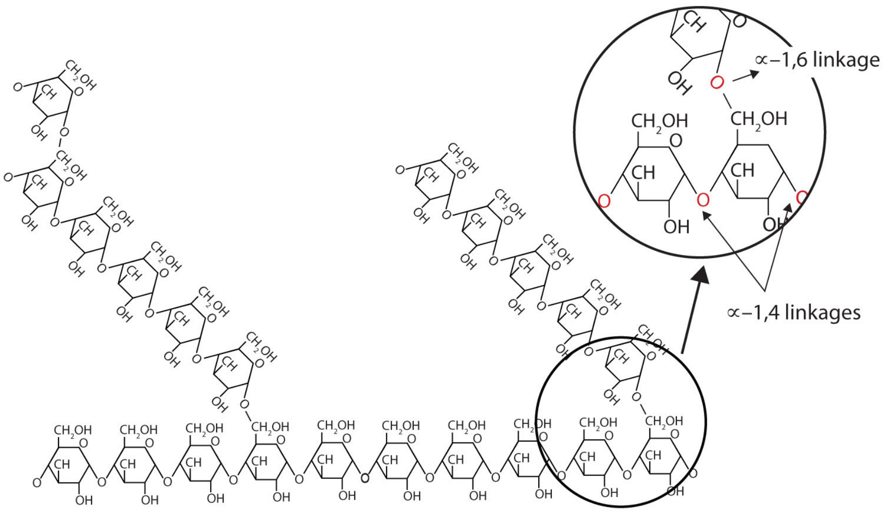


Figure 13.8.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

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.

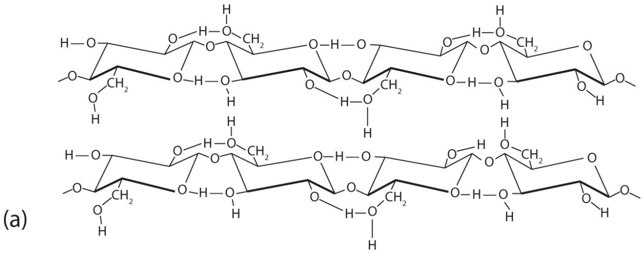


Figure 13.8.3: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

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.

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.

CHAPTER OVERVIEW

14: Lipids

The lipids are a large and diverse group of naturally occurring organic compounds that are related by their solubility in nonpolar organic solvents (e.g., ether, chloroform, acetone and benzene) and general insolubility in water. There is great structural variety among the lipids, as will be demonstrated in the following sections.

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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.

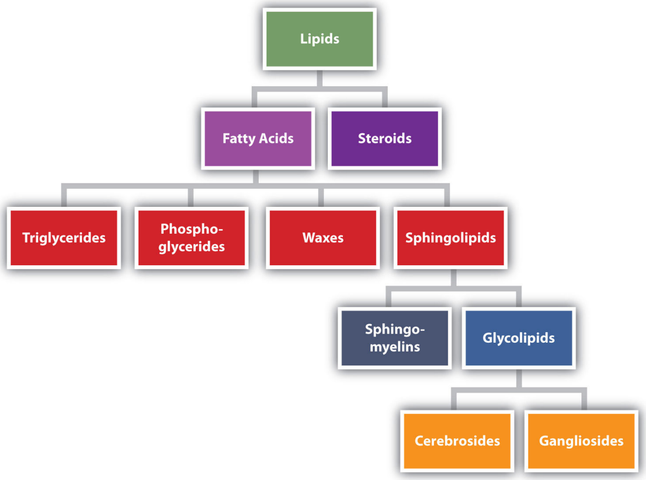


Figure 14.1.1: Lipid Organization Based on Structural Relationships

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.

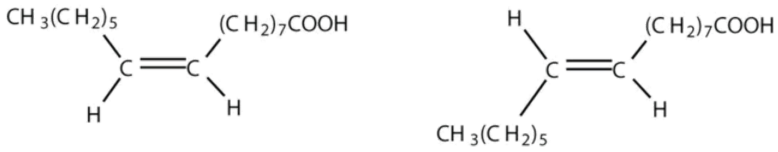
- **17.0: Prelude to Lipids** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.

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 acid

trans fatty acid

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

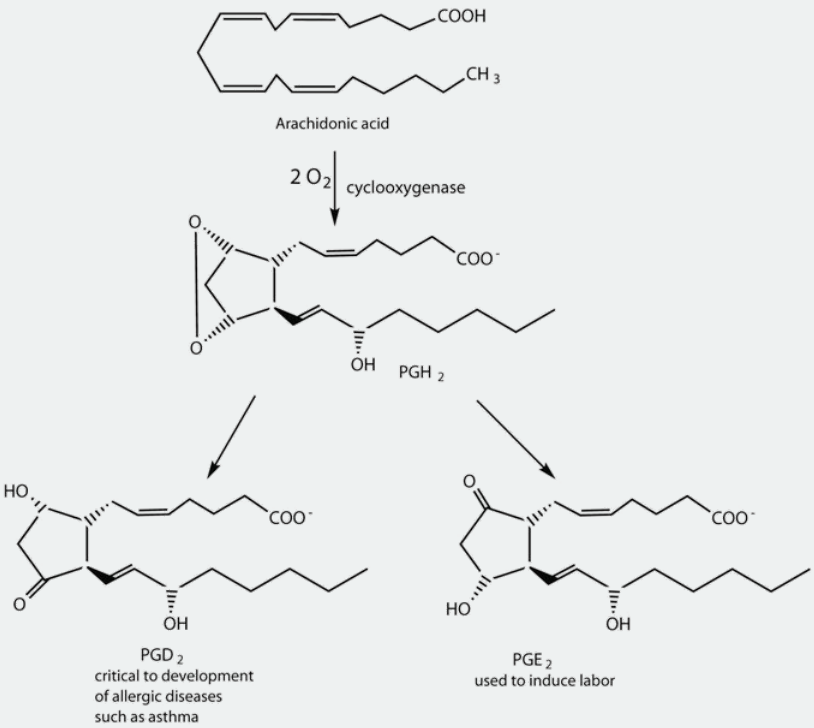
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
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 $14.2.2a$). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure $14.2.2b$). 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.

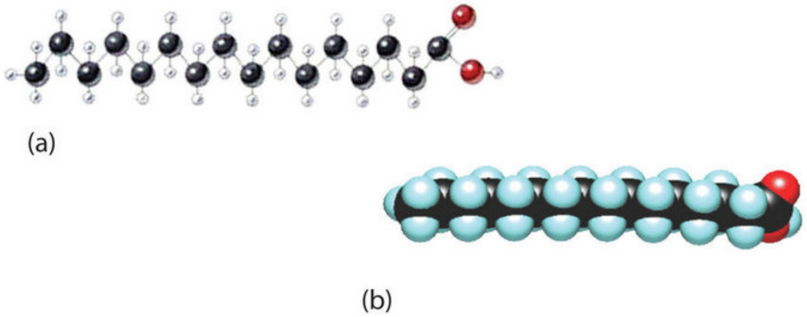
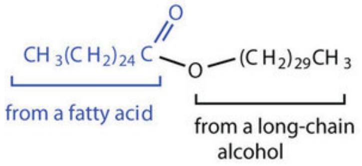


Figure 14.2.2: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

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.

14.3: Fats and Oils

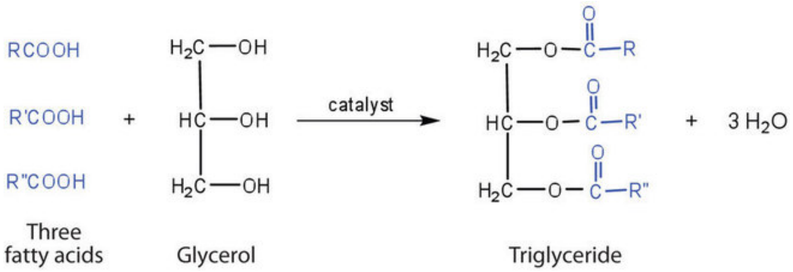
Learning Objectives

- 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.

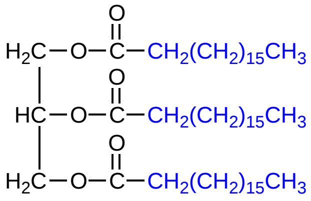
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

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:

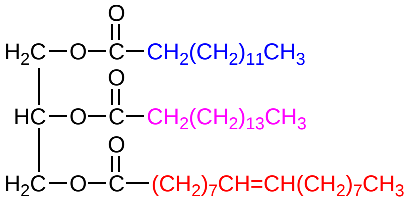


If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring 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

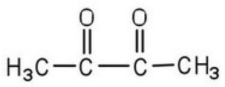
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†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.

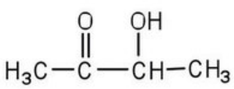
Physical Properties of Fats and Oils

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.



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Diacetyl



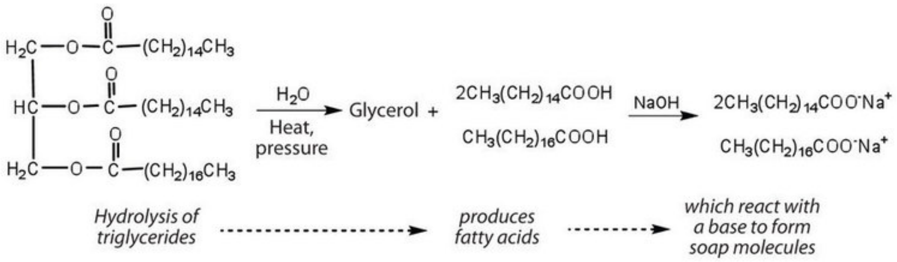
$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3$$

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

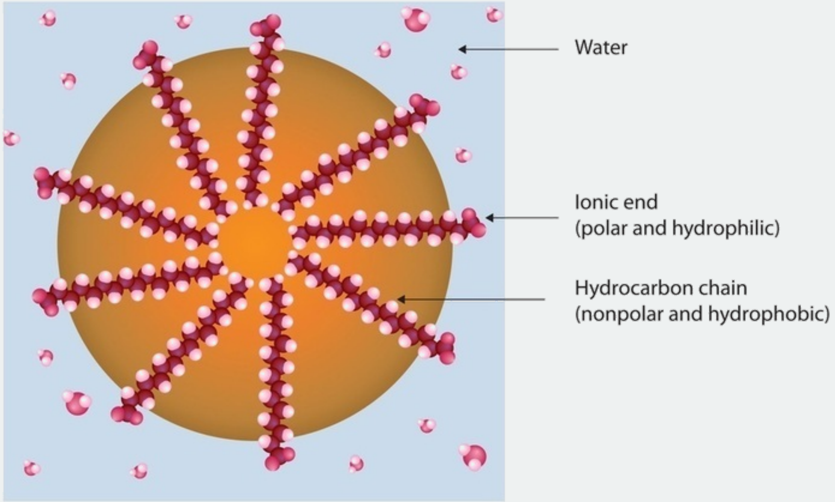
Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called 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

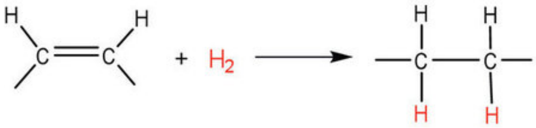
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, 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.

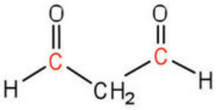
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* 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

$$\sim CH{=}CH{-}CH_2{-}CH{=}CH\sim$$

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.

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 $14.4.1A$) and animal cells (Figure $14.4.1B$) 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.

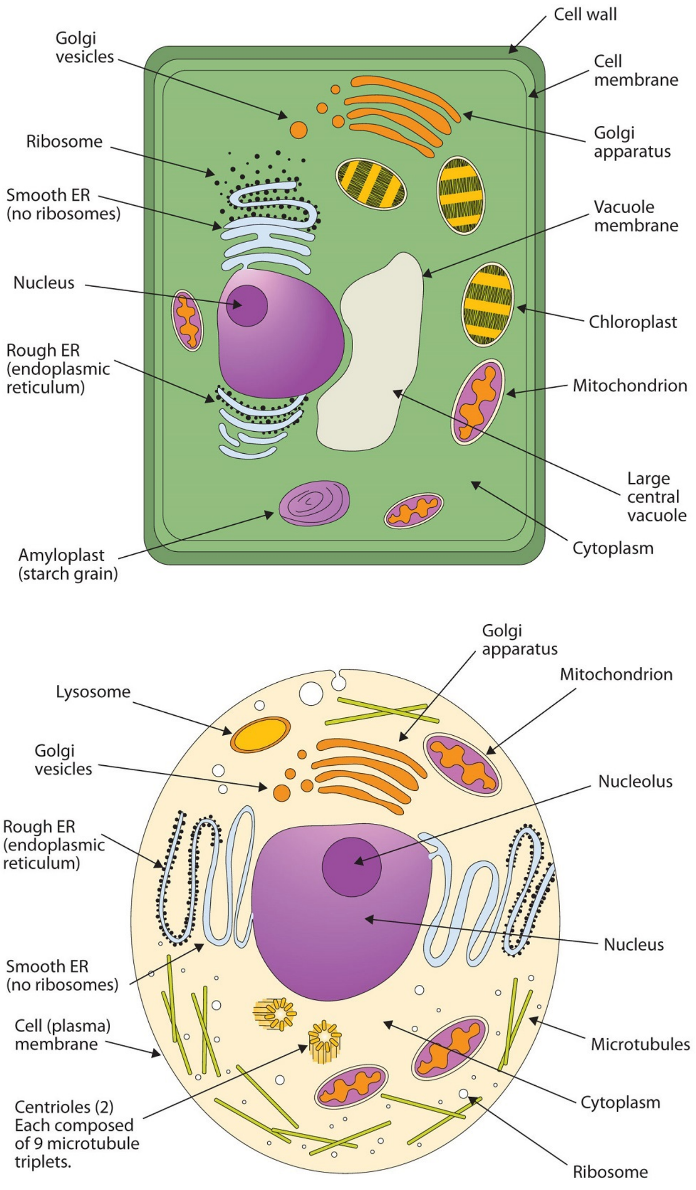


Figure 14.4.1: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

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 $14.4.2$).

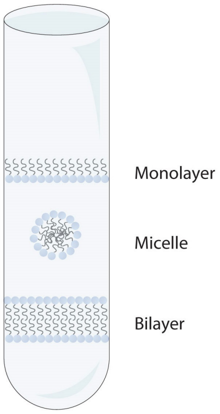


Figure 14.4.2: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

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 $14.4.3$).

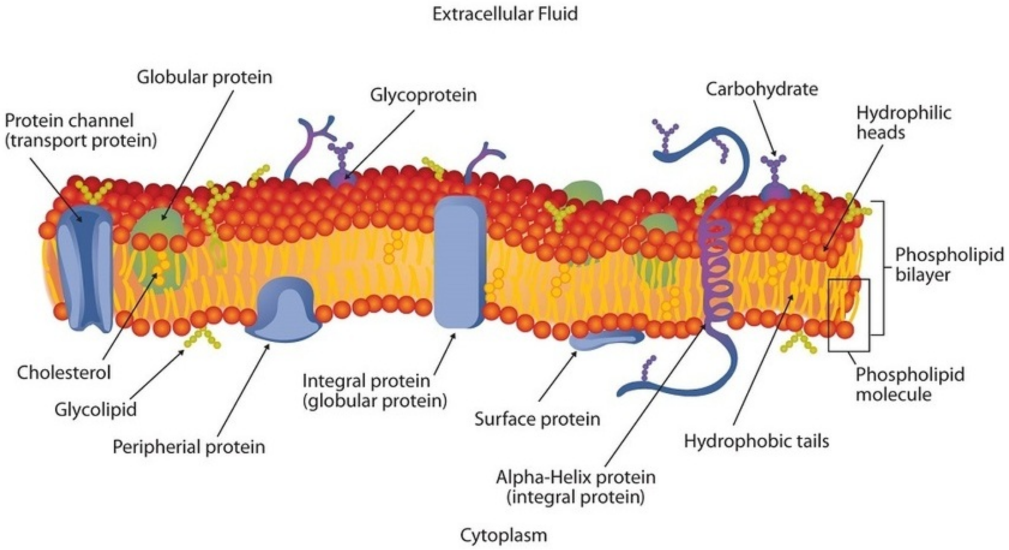


Figure 14.4.3: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

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.

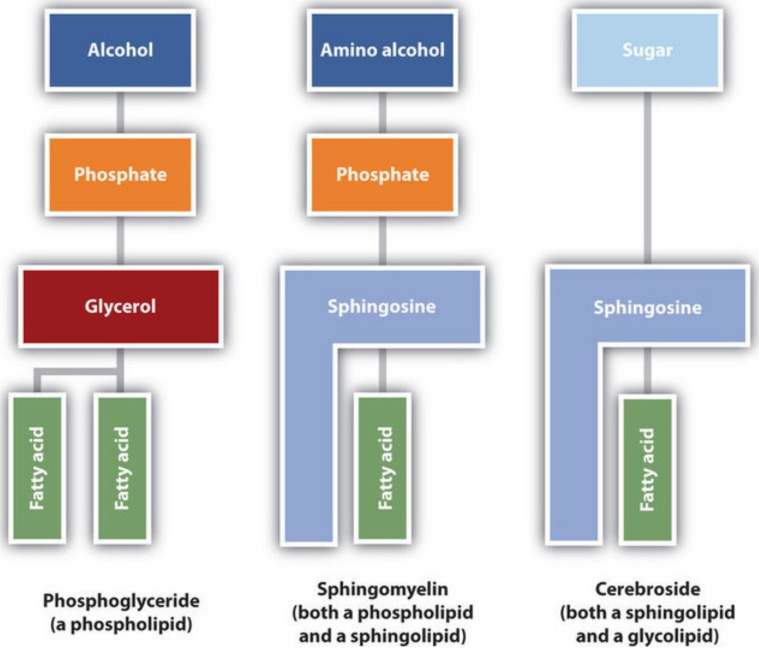


Figure 14.4.4: Component Structures of Some Important Membrane Lipids

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).

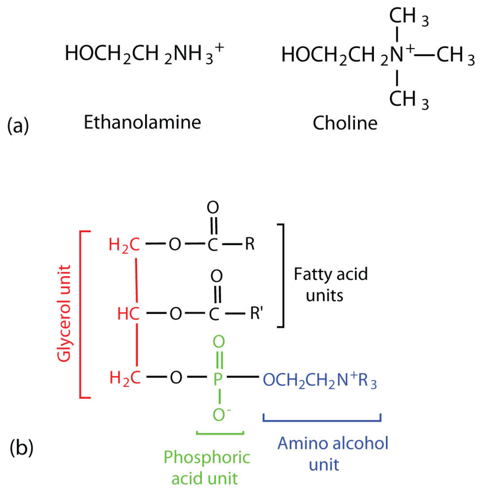
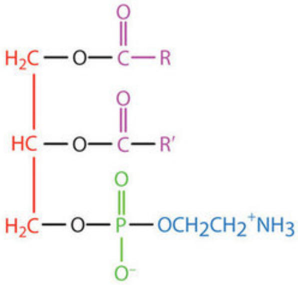


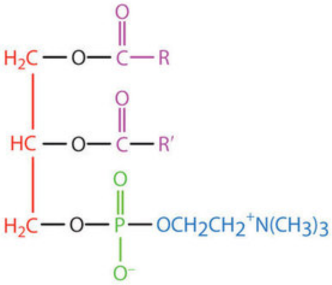
Figure 14.4.5: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

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.

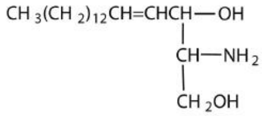


Phosphatidylethanolamine
(cephalin)

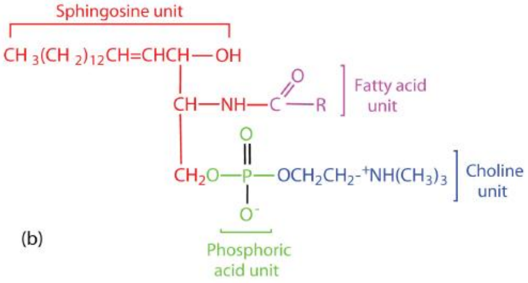


Phosphatidycholine
(lecithin)

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.



(a) Sphingosine



(b)

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.

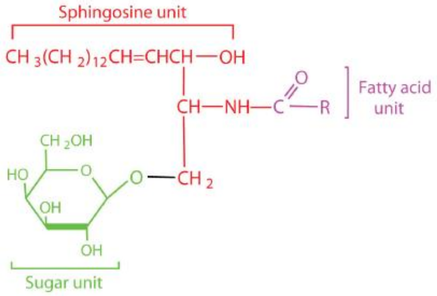


Figure 14.4.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

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

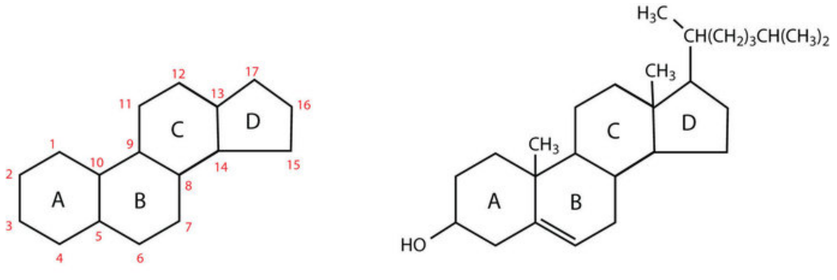
Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

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).



(a) Steroid skeleton

(b) Cholesterol

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 14.5.1a. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 14.5.1b) 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."

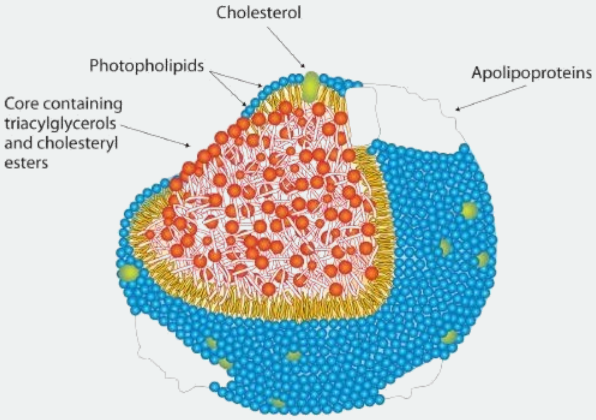
Figure 14.5.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

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.

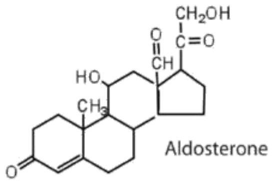
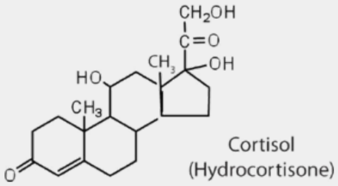
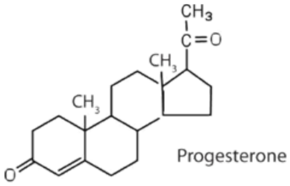
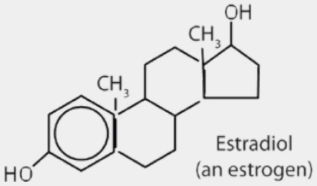
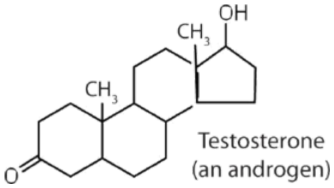
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount 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

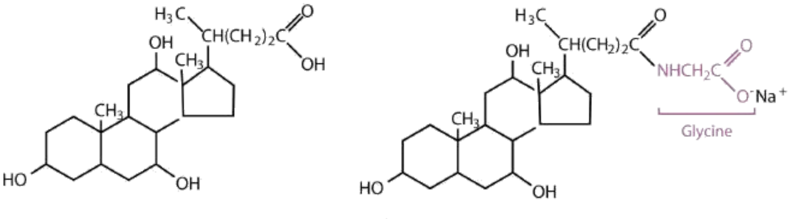
Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female 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.



(a) Cholic acid (a bile acid) (b) Sodium glycocholate (a bile salt)

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.

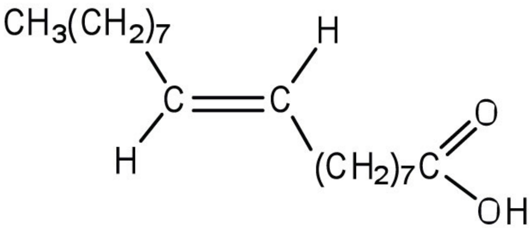
Summary

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.

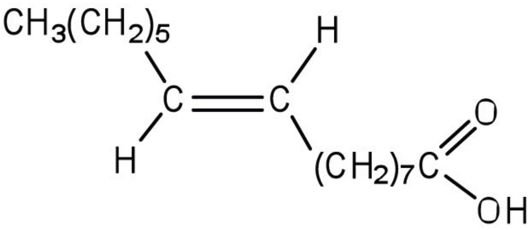
14.E: Exercises

Additional Exercises

1. The melting point of elaidic acid is 52°C.
   a. What trend is observed when comparing the melting points of elaidic acid, oleic acid, and stearic acid? Explain.
   b. Would you expect the melting point of palmitelaidic acid to be lower or higher than that of elaidic acid? Explain.

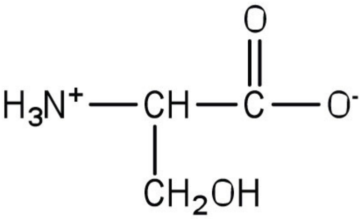


Elaidic acid



Palmitelaidic acid

2. Examine the labels on two brands of margarine and two brands of shortening and list the oils used in the various brands.
3. Draw a typical lecithin molecule that incorporates glycerol, palmitic acid, oleic acid, phosphoric acid, and choline. Circle all the ester bonds.
4. In cerebrosides, is the linkage between the fatty acid and sphingosine an amide bond or an ester bond? Justify your answer.
5. Serine is an amino acid that has the following structure. Draw the structure for a phosphatidylserine that contains a palmitic acid and a palmitoleic acid unit.

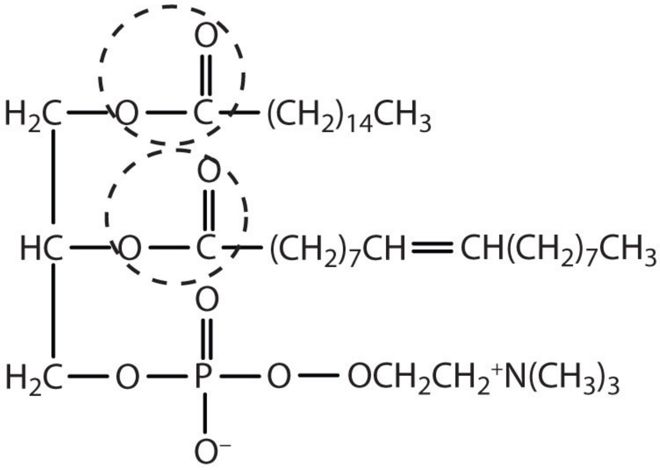


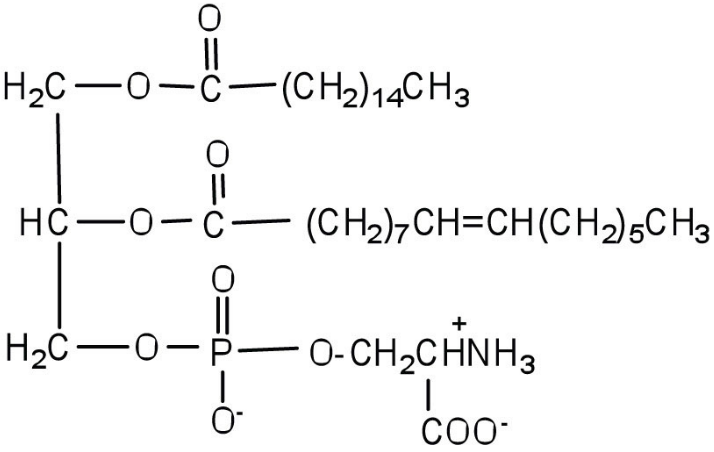
$H_3N^+-CH(CH_2OH)-C(=O)-O^-$

6. Explain whether each compound would be expected to diffuse through the lipid bilayer of a cell membrane.
   a. potassium chloride
   b. $CH_3CH_2CH_2CH_2CH_2CH_3$
   c. fructose
7. Identify the role of each steroid hormone in the body.
   a. progesterone
   b. aldosterone
   c. testosterone
   d. cortisol
8. How does the structure of cholic acid differ from that of cholesterol? Which compound would you expect to be more polar? Why?
9. a. What fatty acid is the precursor for the prostaglandins?
   b. Identify three biological effects of prostaglandins.
10. Why is it important to determine the ratio of LDLs to HDLs, rather than just the concentration of serum cholesterol?

Answers

1. a. Stearic acid has the highest melting point, followed by elaidic acid, and then oleic acid with the lowest melting point. Elaidic acid is a *trans* fatty acid, and the carbon chains can pack together almost as tightly as those of the saturated stearic acid. Oleic acid is a *cis* fatty acid, and the bend in the hydrocarbon chain keeps these carbon chains from packing as closely together; fewer interactions lead to a much lower melting point.
   b. The melting point of palmitelaidic acid should be lower than that of elaidic acid because it has a shorter carbon chain (16, as compared to 18 for elaidic acid). The shorter the carbon chain, the lower the melting point due to a decrease in intermolecular interactions.

3. 

5. 

7. a. regulates the menstrual cycle and maintains pregnancy
   b. regulates salt metabolism by stimulating the kidneys to retain sodium and excrete potassium
   c. stimulates and maintains male sex characteristics
   d. stimulates the conversion of proteins to carbohydrates

9. a. arachidonic acid
   b. induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response

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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.

CHAPTER OVERVIEW

15: Amino Acids and Proteins

Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

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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).

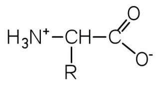
15.2: Properties of Amino Acids

Learning Objectives

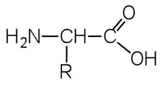
- To recognize amino acids and classify them based on the characteristics of their side chains.

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

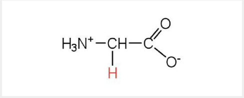
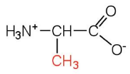
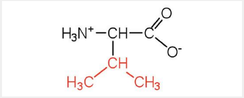
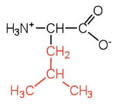


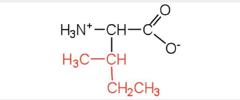
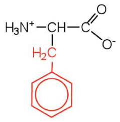
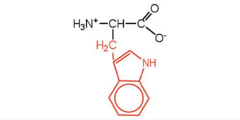
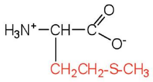
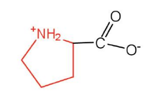
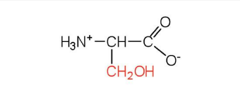
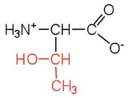
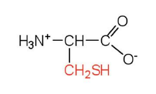
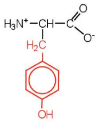
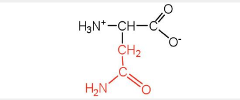
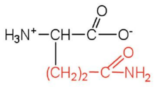
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

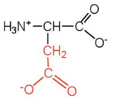
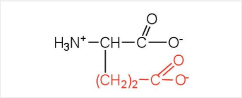
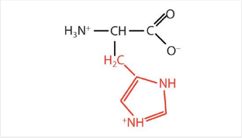
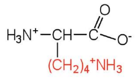
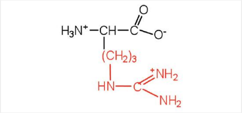
Classification

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.

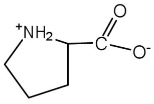
Table 15.2.1: Common Amino Acids Found in Proteins

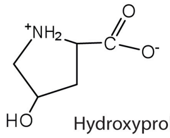
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

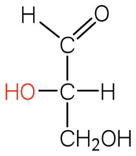
The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning "sweet"). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.


Proline

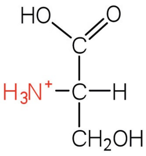

Hydroxyproline

Configuration

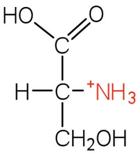
Notice in Table 15.2.1 that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as 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.



L–(–)–Glyceraldehyde



L–Amino acid



D–Amino acid

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

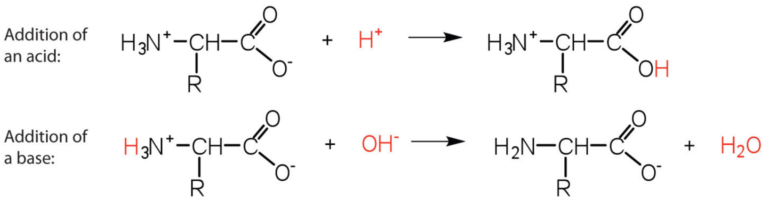
Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

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.

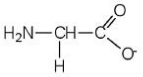


Example 15.3.1

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.

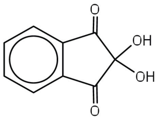
The particular pH at which a given amino acid exists in solution as a zwitterion is called the isoelectric point (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have 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: Examples of Some Representative Amino Acids

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7

Amino Acid	Classification	pI
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

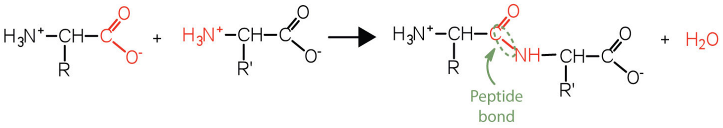
Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

15.4: Peptides

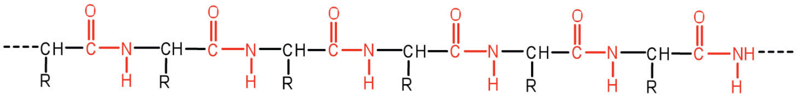
Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

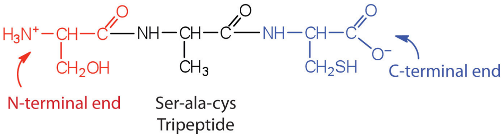
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water 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.

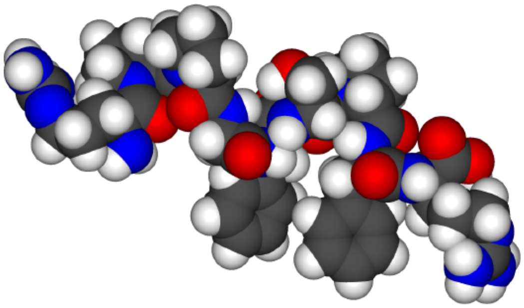


Figure 15.4.1: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

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).

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 $15.5.1$.

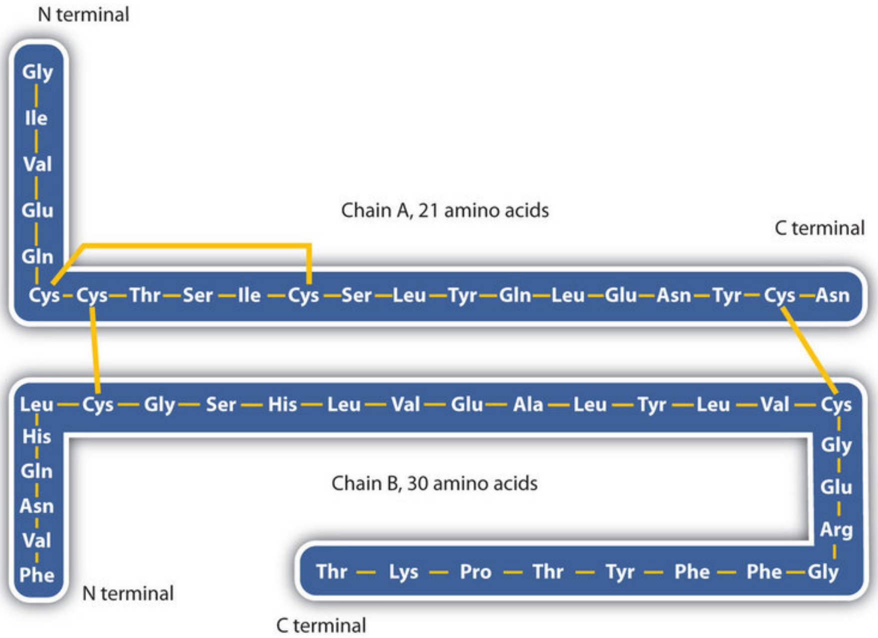


Figure 15.5.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

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.

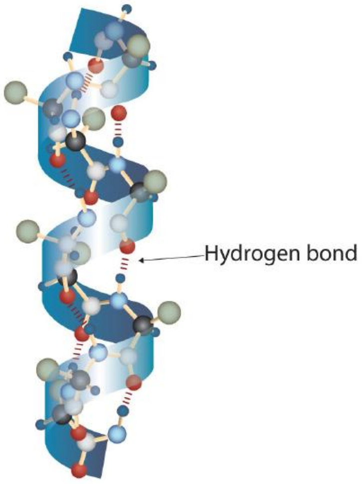


Figure 15.5.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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.

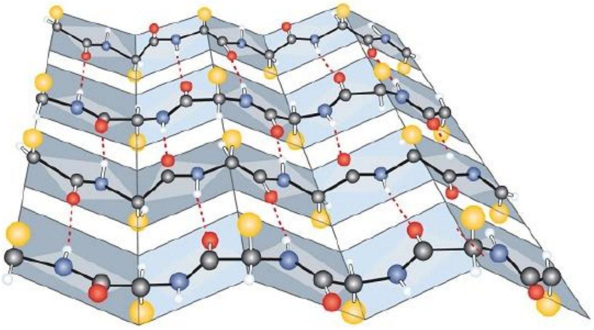


Figure 15.5.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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.

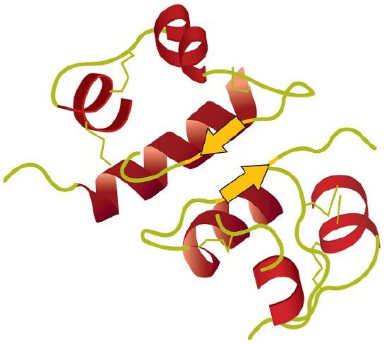
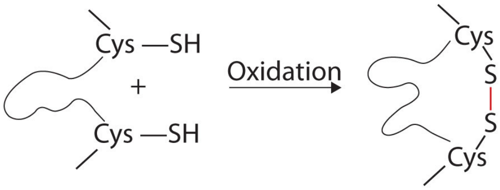


Figure 15.5.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

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.

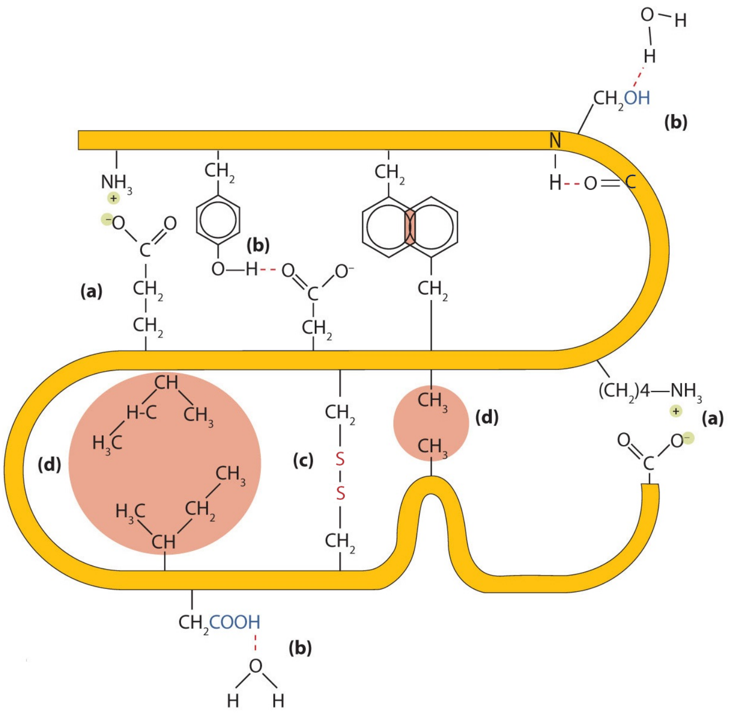


Figure 15.5.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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.

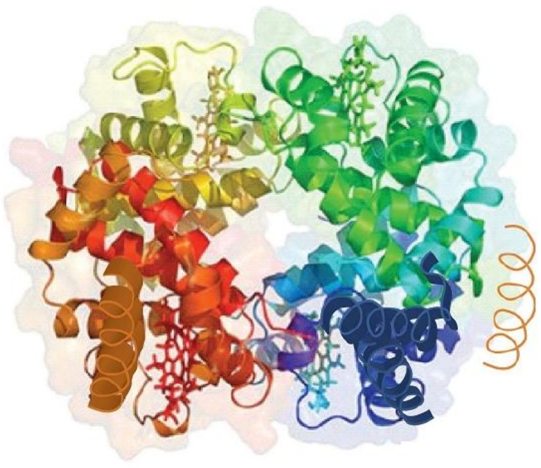


Figure 15.5.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

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).

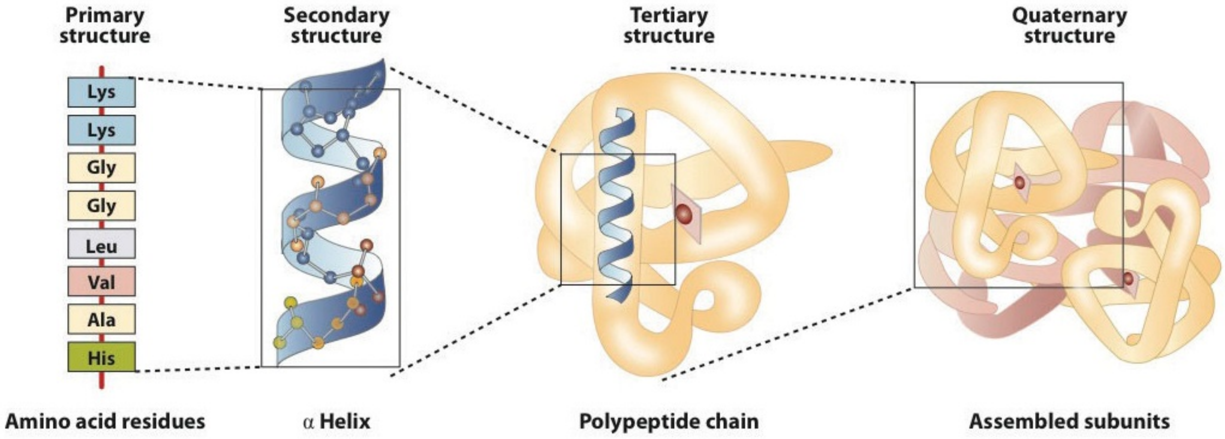


Figure 15.5.7: Levels of Structure in Proteins

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.

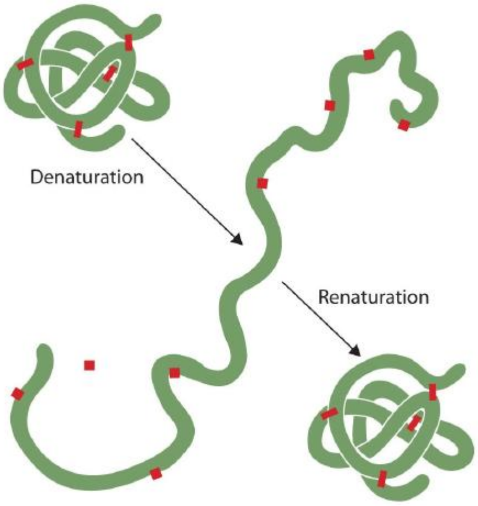


Figure 15.5.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

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.

CHAPTER OVERVIEW

16: Nucleic Acids

The blueprint for the reproduction and the maintenance of each organism is found in the nuclei of its cells, concentrated in elongated, threadlike structures called chromosomes. These complex structures, consisting of DNA and proteins, contain the basic units of heredity, called genes. The number of chromosomes (and genes) varies with each species. Human body cells have 23 pairs of chromosomes having 20,000–40,000 different genes.

Sperm and egg cells contain only a single copy of each chromosome; that is, they contain only one member of each chromosome pair. Thus, in sexual reproduction, the entire complement of chromosomes is achieved only when an egg and sperm combine. A new individual receives half its hereditary material from each parent. Calling the unit of heredity a “gene” merely gives it a name. But what really are genes and how is the information they contain expressed? One definition of a gene is that it is a segment of DNA that constitutes the code for a specific polypeptide. If genes are segments of DNA, we need to learn more about the structure and physiological function of DNA. We begin by looking at the small molecules needed to form DNA and RNA (ribonucleic acid)—the nucleotides.

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16.1: Prelude to Nucleic Acids

Following the initial isolation of insulin in 1921, diabetic patients could be treated with insulin obtained from the pancreases of cattle and pigs. Unfortunately, some patients developed an allergic reaction to this insulin because its amino acid sequence was not identical to that of human insulin. In the 1970s, an intense research effort began that eventually led to the production of genetically engineered human insulin—the first genetically engineered product to be approved for medical use. To accomplish this feat, researchers first had to determine how insulin is made in the body and then find a way of causing the same process to occur in nonhuman organisms, such as bacteria or yeast cells. Many aspects of these discoveries are presented in this chapter on nucleic acids.

Figure 16.1.1: A vial of insulin. It has been given a trade name, Actrapid, by the manufacturer. (Public Domain; Mr Hyde).

16.2: Nucleotides

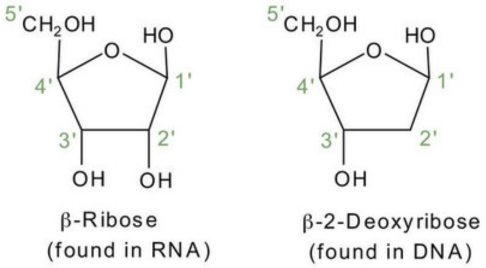
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3 × 10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure 16.2.1).

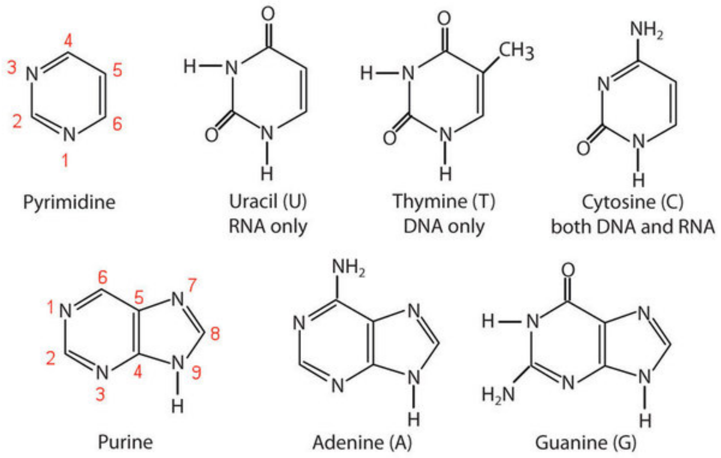


Figure 16.2.1: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table 16.2.1 summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table 16.2.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure $16.2.2$

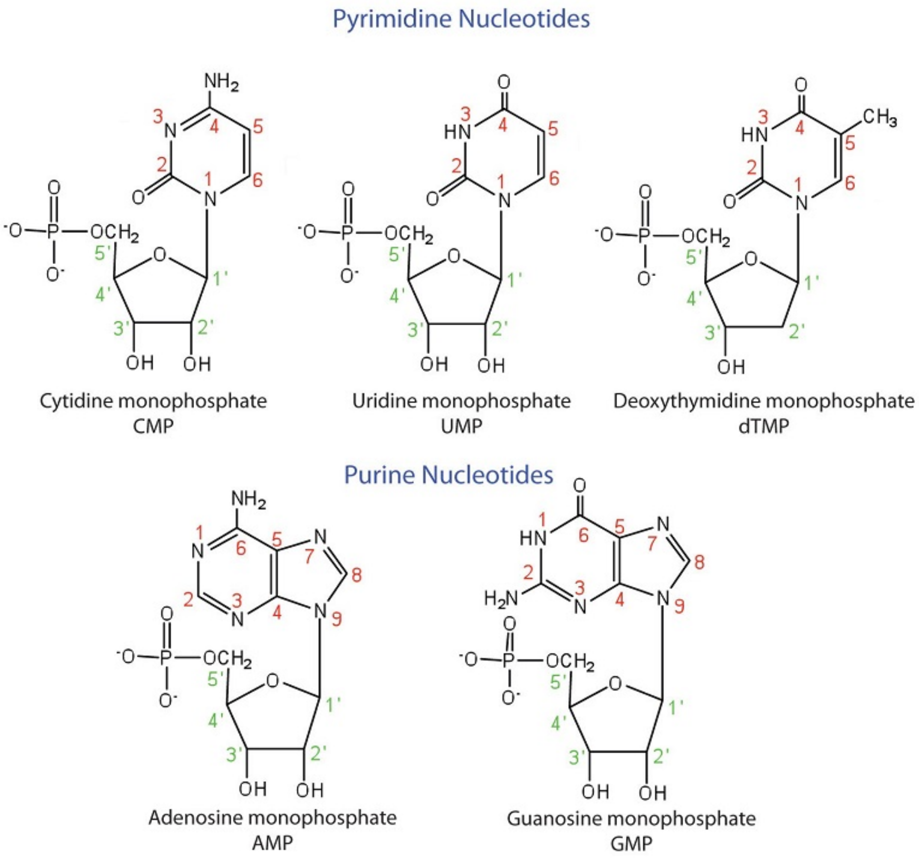


Figure 16.2.2: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure $16.2.3$, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

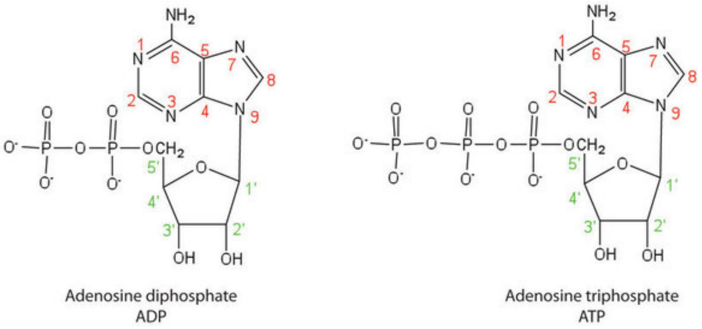


Figure 16.2.3: Structures of Two Important Adenine-Containing Nucleotides

Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

16.3: Nucleic Acid Structure

Skills to Develop

- Identify the two types of nucleic acids and the function of each type.
- Describe how nucleotides are linked together to form nucleic acids.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure $16.3.1$). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

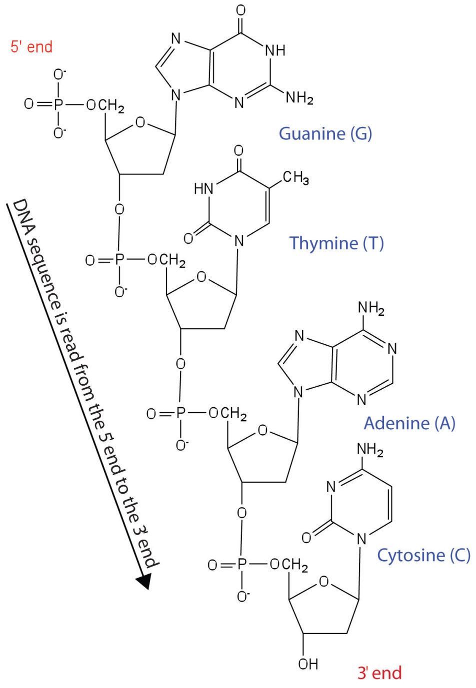


Figure $\mathbf{16.3.1}$ *Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2', and uracil would replace thymine.*

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure $16.3.1$) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 16.3.1 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 16.3.2).

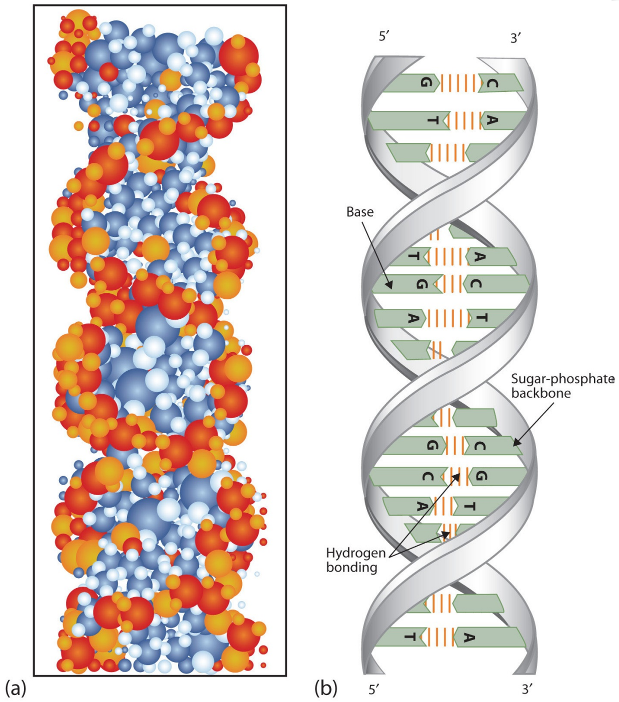


Figure 16.3.2 DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 16.3.3 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

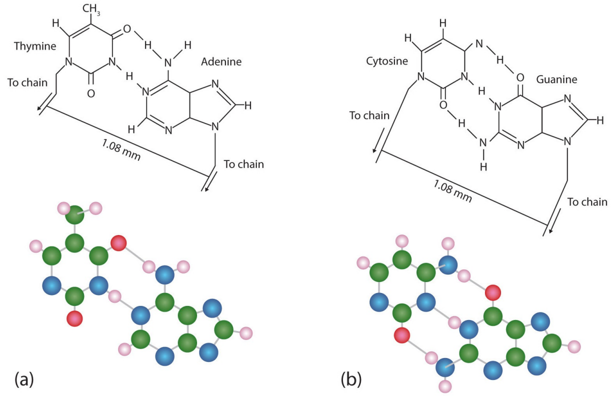


***Figure* $16.3.3$** *Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.*

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure $16.3.4$ If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure $16.3.3$ is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

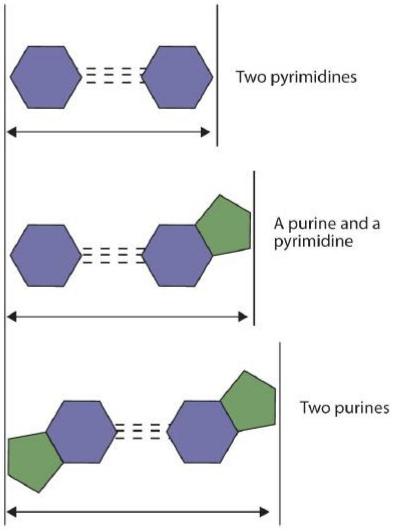


***Figure* $16.3.4$** *Difference in Widths of Possible Base Pairs*

Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

Concept Review Exercises

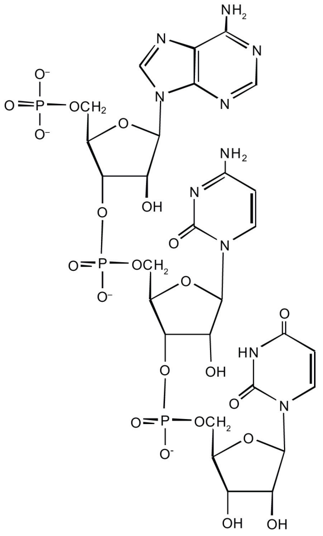
1.
    a. Name the two kinds of nucleic acids.
    b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

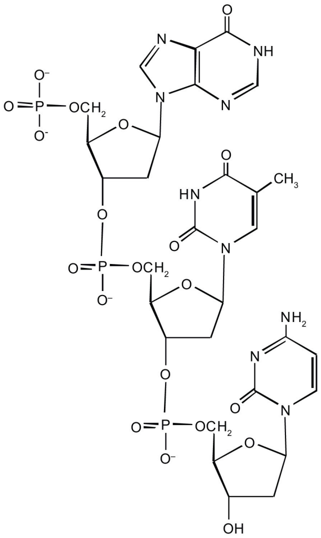
1.
    a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
    b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

1. For this short RNA segment,
    a. identify the 5′ end and the 3′ end of the molecule.
    b. circle the atoms that comprise the backbone of the nucleic acid chain.
    c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
    a. identify the 5′ end and the 3′ end of the molecule.
    b. circle the atoms that comprise the backbone of the nucleic acid chain.
    c. write the nucleotide sequence of this DNA segment.

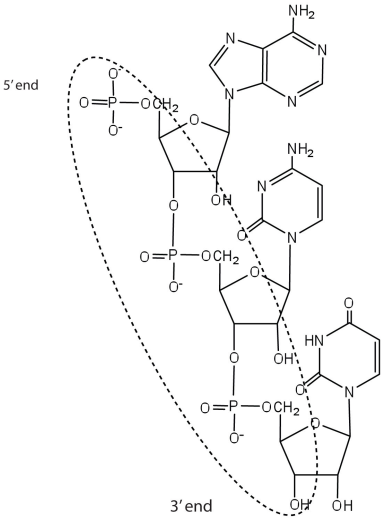


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
   a. cytosine
   b. adenine
   c. guanine
   d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
   a. cytosine
   b. adenine
   c. guanine
   d. thymine
5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′
6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers



1.

   c. ACU

3.

   a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

16.4: Replication and Expression of Genetic Information

Learning Objectives

- Describe how a new copy of DNA is synthesized.
- Describe how RNA is synthesized from DNA.
- Identify the different types of RNA and the function of each type of RNA.

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is "unzipped," so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme, recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure 16.4.1). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

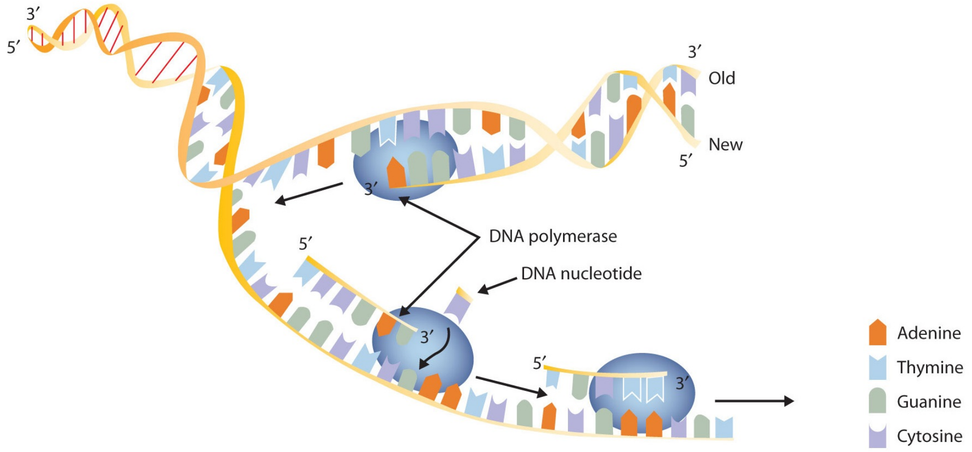


Figure 16.4.1: A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

Example 16.4.1

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

> Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′ (can also be written as TCAACTCATGGA).

> **? Exercise 16.4.1**
>
> A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

What do we mean when we say information is encoded in the DNA molecule? An organism's DNA can be compared to a book containing directions for assembling a model airplane or for knitting a sweater. Letters of the alphabet are arranged into words, and these words direct the individual to perform certain operations with specific materials. If all the directions are followed correctly, a model airplane or sweater is produced.

In DNA, the particular sequences of nucleotides along the chains encode the directions for building an organism. Just as *saw* means one thing in English and *was* means another, the sequence of bases CGT means one thing, and TGC means something different. Although there are only four letters—the four nucleotides—in the genetic code of DNA, their sequencing along the DNA strands can vary so widely that information storage is essentially unlimited.

Transcription

For the hereditary information in DNA to be useful, it must be "expressed," that is, used to direct the growth and functioning of an organism. The first step in the processes that constitute DNA expression is the synthesis of RNA, by a template mechanism that is in many ways analogous to DNA replication. Because the RNA that is synthesized is a complementary copy of information contained in DNA, RNA synthesis is referred to as transcription. There are three key differences between replication and transcription:

1. RNA molecules are much shorter than DNA molecules; only a portion of one DNA strand is copied or transcribed to make an RNA molecule.
2. RNA is built from ribonucleotides rather than deoxyribonucleotides.
3. The newly synthesized RNA strand does not remain associated with the DNA sequence it was transcribed from.

The DNA sequence that is transcribed to make RNA is called the *template strand*, while the complementary sequence on the other DNA strand is called the *coding* or *informational strand*. To initiate RNA synthesis, the two DNA strands unwind at specific sites along the DNA molecule. Ribonucleotides are attracted to the uncoiling region of the DNA molecule, beginning at the 3′ end of the template strand, according to the rules of base pairing. Thymine in DNA calls for adenine in RNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil. RNA polymerase—an enzyme—binds the complementary ribonucleotide and catalyzes the formation of the ester linkage between ribonucleotides, a reaction very similar to that catalyzed by DNA polymerase (Figure 16.4.2). Synthesis of the RNA strand takes place in the 5′ to 3′ direction, antiparallel to the template strand. Only a short segment of the RNA molecule is hydrogen-bonded to the template strand at any time during transcription. When transcription is completed, the RNA is released, and the DNA helix reforms. The nucleotide sequence of the RNA strand formed during transcription is identical to that of the corresponding coding strand of the DNA, except that U replaces T.

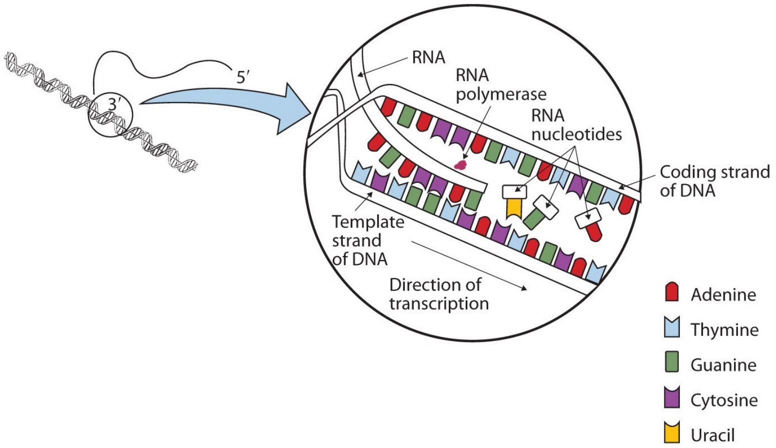


Figure 16.4.2: A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.

✓ Example 16.4.2

A portion of the template strand of a gene has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Solution

Four things must be remembered in answering this question: (1) the DNA strand and the RNA strand being synthesized are antiparallel; (2) RNA is synthesized in a 5′ to 3′ direction, so transcription begins at the 3′ end of the template strand; (3) ribonucleotides are used in place of deoxyribonucleotides; and (4) thymine (T) base pairs with adenine (A), A base pairs with uracil (U; in RNA), and cytosine (C) base pairs with guanine (G). The sequence is determined to be 3′-AGGUACUCAACU-5′ (can also be written as 5′-UCAACUCAUGGA-3′).

? Exercise 16.4.2

A portion of the template strand of a gene has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Three types of RNA are formed during transcription: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). These three types of RNA differ in function, size, and percentage of the total cell RNA (Table 16.4.1). mRNA makes up only a small percent of the total amount of RNA within the cell, primarily because each molecule of mRNA exists for a relatively short time; it is continuously being degraded and resynthesized. The molecular dimensions of the mRNA molecule vary according to the amount of genetic information a given molecule contains. After transcription, which takes place in the nucleus, the mRNA passes into the cytoplasm, carrying the genetic message from DNA to the ribosomes, the sites of protein synthesis. Elsewhere, we shall see how mRNA directly determines the sequence of amino acids during protein synthesis.

Table 16.4.1: Properties of Cellular RNA in Escherichia coli

Type	Function	Approximate Number of Nucleotides	Percentage of Total Cell RNA
mRNA	codes for proteins	100–6,000	~3
rRNA	component of ribosomes	120–2900	83
tRNA	adapter molecule that brings the amino acid to the ribosome	75–90	14

Ribosomes are cellular substructures where proteins are synthesized. They contain about 65% rRNA and 35% protein, held together by numerous noncovalent interactions, such as hydrogen bonding, in an overall structure consisting of two globular particles of unequal size.

Molecules of tRNA, which bring amino acids (one at a time) to the ribosomes for the construction of proteins, differ from one another in the kinds of amino acid each is specifically designed to carry. A set of three nucleotides, known as a codon, on the mRNA determines which kind of tRNA will add its amino acid to the growing chain. Each of the 20 amino acids found in proteins has at least one corresponding kind of tRNA, and most amino acids have more than one.

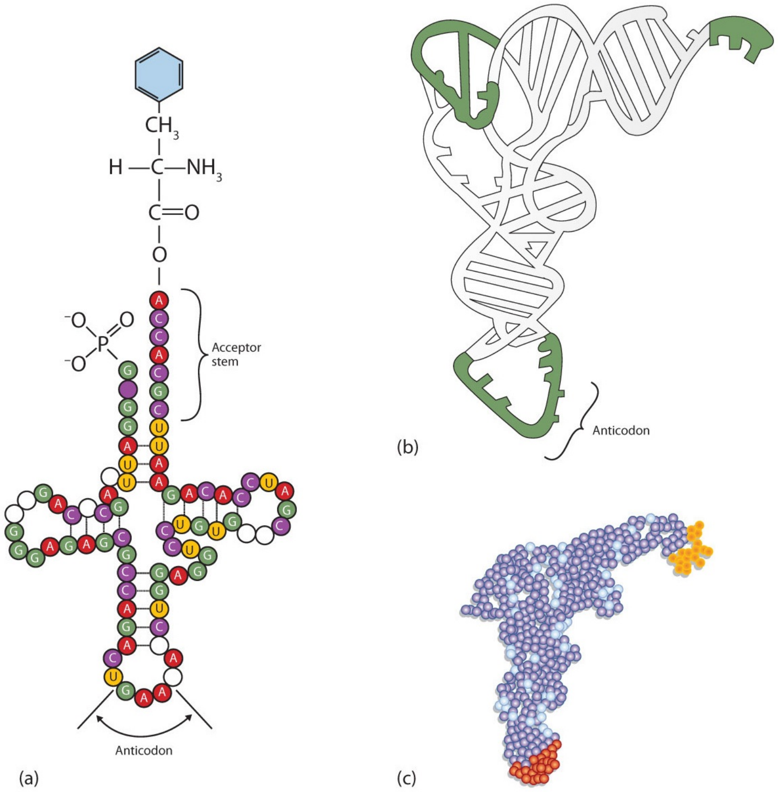


Figure 16.4.3: Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the $3'$ end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of the four common ribonucleotides A, U, C, and G.) (b) In the three-dimensional structure of yeast phenylalanine tRNA, note that the anticodon loop is at the bottom and the acceptor stem is at the top right. (c) This shows a space-filling model of the tRNA.

The two-dimensional structure of a tRNA molecule has three distinctive loops, reminiscent of a cloverleaf (Figure 16.4.3). On one loop is a sequence of three nucleotides that varies for each kind of tRNA. This triplet, called the anticodon, is complementary to and pairs with the codon on the mRNA. At the opposite end of the molecule is the acceptor stem, where the amino acid is attached.

Summary

- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.
- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- Three types of RNA are formed during transcription: mRNA, rRNA, and tRNA.

16.5: Protein Synthesis and the Genetic Code

Learning Objectives

- describe the characteristics of the genetic code.
- describe how a protein is synthesized from mRNA.

One of the definitions of a gene is as follows: a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are 4^2, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is 4^3, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.

***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see VCell, NDSU(opens in new window) [vcell.ndsu.nodak.edu]*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

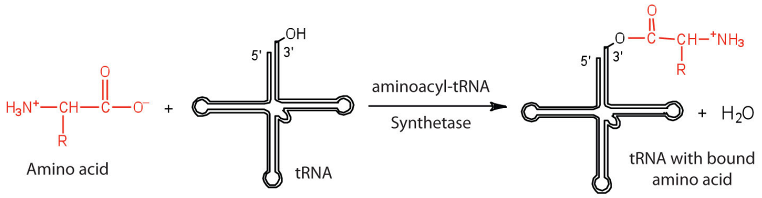


Figure 16.5.1: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure 16.5.1). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. Figure 16.5.2 depicts a schematic stepwise representation of this all-important process.

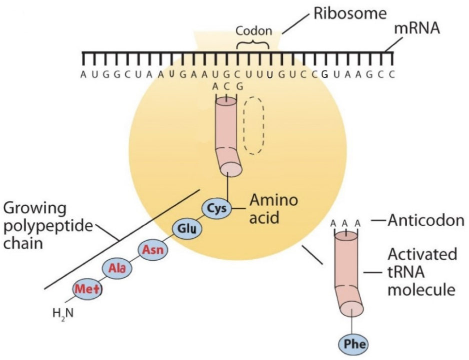


Figure 16.5.2*a*: The Elongation Steps in Protein Synthesis - Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

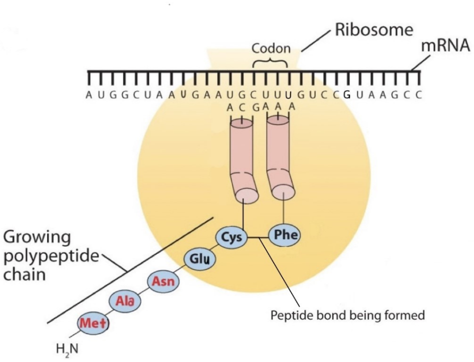


Figure 16.5.2*b*: The Elongation Steps in Protein Synthesis - An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though basepairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide chain by the formation of a peptide linkage between the carboxyl group of Cys and the amino acid group of the Phe. This reaction is catalyzed by the enzyme peptidyl transferase, a component of the ribosome.

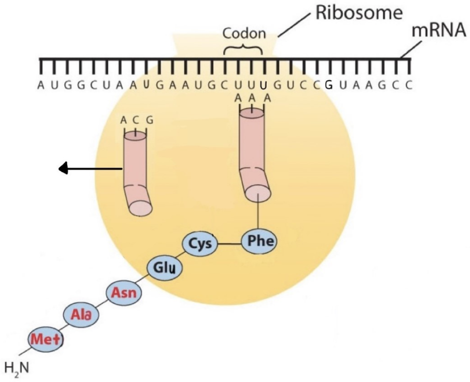


Figure 16.5.2*c*: The Elongation Steps in Protein Synthesis - The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

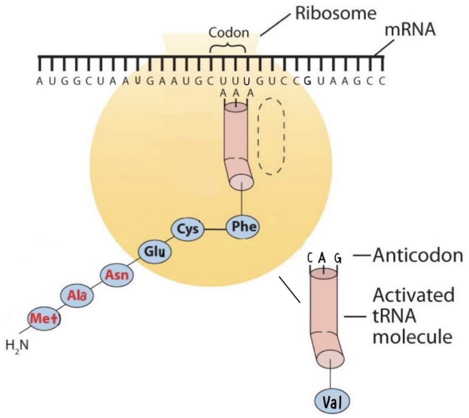
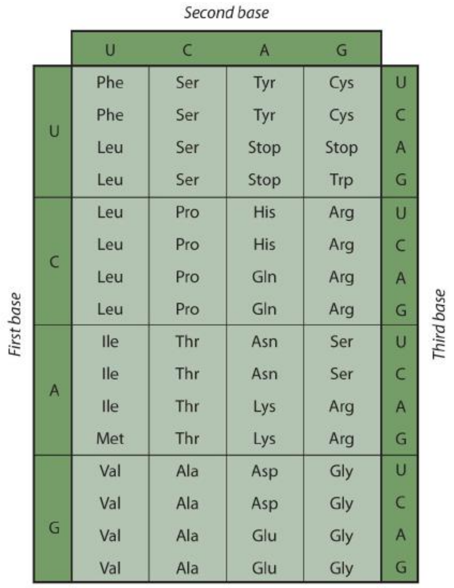


Figure 16.5.2d: The Elongation Steps in Protein Synthesis - The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)-(d) will be repeated until the ribosome reaches a stop codon.

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 16.5.3, shows that 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.



	Second base				
First base	U	C	A	G	Third base
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Stop	Stop	A
	Leu	Ser	Stop	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

Figure 16.5.3: The Genetic Code

✓ Example 16.5.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

Solution

Use Figure 16.5.3 to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid. The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

Exercise 16.5.4

A portion of an RNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan), more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.
5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.
6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

Summary

In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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16.6: Mutations and Genetic Diseases

Learning Objectives

- To describe the causes of genetic mutations and how they lead to genetic diseases.

We have seen that the sequence of nucleotides in a cell's deoxyribonucleic acid (DNA) is what ultimately determines the sequence of amino acids in proteins made by the cell and thus is critical for the proper functioning of the cell. On rare occasions, however, the nucleotide sequence in DNA may be modified either spontaneously (by errors during replication, occurring approximately once for every 10 billion nucleotides) or from exposure to heat, radiation, or certain chemicals. Any chemical or physical change that alters the nucleotide sequence in DNA is called a mutation. When a mutation occurs in an egg or sperm cell that then produces a living organism, it will be inherited by all the offspring of that organism.

Common types of mutations include **substitution** (a different nucleotide is substituted), **insertion** (the addition of a new nucleotide), and **deletion** (the loss of a nucleotide). These changes within DNA are called point mutations because only one nucleotide is substituted, added, or deleted (Figure 16.6.1). Because an insertion or deletion results in a frame-shift that changes the reading of subsequent codons and, therefore, alters the entire amino acid sequence that follows the mutation, insertions and deletions are usually more harmful than a substitution in which only a single amino acid is altered.

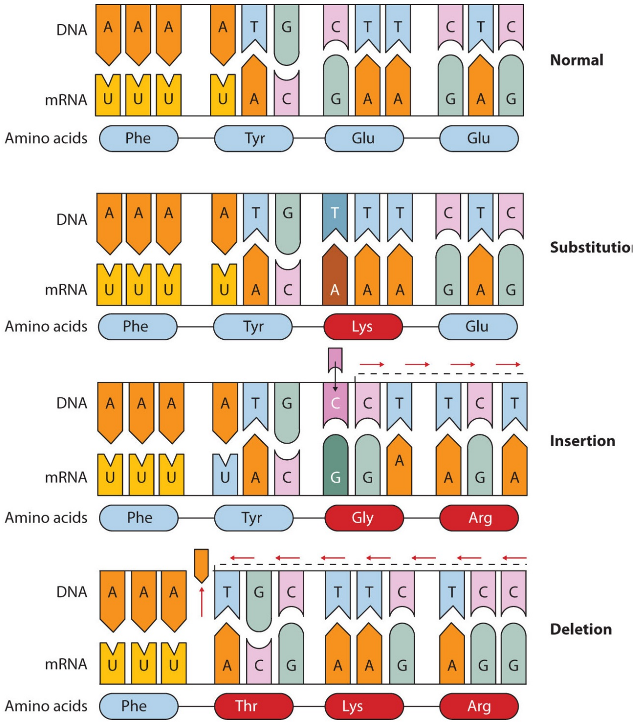


Figure 16.6.1: Three Types of Point Mutations

The chemical or physical agents that cause mutations are called mutagens. Examples of physical mutagens are ultraviolet (UV) and gamma radiation. Radiation exerts its mutagenic effect either directly or by creating free radicals that in turn have mutagenic effects. Radiation and free radicals can lead to the formation of bonds between nitrogenous bases in DNA. For example, exposure to UV light can result in the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer (Figure 16.6.2). If not repaired, the dimer prevents the formation of the double helix at the point where it occurs. The genetic disease *xeroderma pigmentosum* is caused by a lack of the enzyme that cuts out the thymine dimers in damaged DNA. Individuals affected by this condition are abnormally sensitive to light and are more prone to skin cancer than normal individuals.

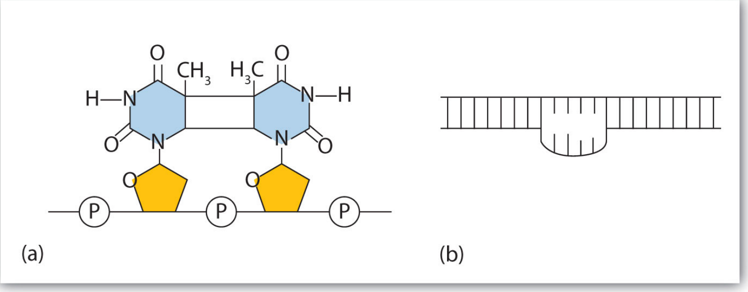


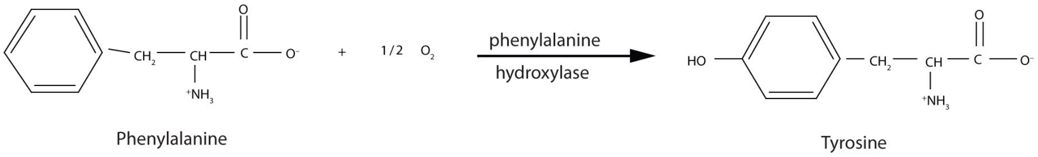
Figure 16.6.2: An Example of Radiation Damage to DNA. (a) The thymine dimer is formed by the action of UV light. (b) When a defect in the double strand is produced by the thymine dimer, this defect temporarily stops DNA replication, but the dimer can be removed, and the region can be repaired by an enzyme repair system.

Sometimes gene mutations are beneficial, but most of them are detrimental. For example, if a point mutation occurs at a crucial position in a DNA sequence, the affected protein will lack biological activity, perhaps resulting in the death of a cell. In such cases the altered DNA sequence is lost and will not be copied into daughter cells. Nonlethal mutations in an egg or sperm cell may lead to metabolic abnormalities or hereditary diseases. Such diseases are called *inborn errors of metabolism* or genetic diseases. A partial listing of genetic diseases is presented in Figure 16.6.1, and two specific diseases are discussed in the following sections. In most cases, the defective gene results in a failure to synthesize a particular enzyme.

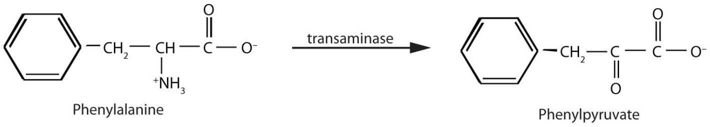
Figure 16.6.1: Some Representative Genetic Diseases in Humans and the Protein or Enzyme Responsible

Disease	Responsible Protein or Enzyme
alkaptonuria	homogentisic acid oxidase
galactosemia	galactose 1-phosphate uridyl transferase, galactokinase, or UDP galactose epimerase
Gaucher disease	glucocerebrosidase
gout and Lesch-Nyhan syndrome	hypoxanthine-guanine phosphoribosyl transferase
hemophilia	antihemophilic factor (factor VIII) or Christmas factor (factor IX)
homocystinuria	cystathionine synthetase
maple syrup urine disease	branched chain α-keto acid dehydrogenase complex
McArdle syndrome	muscle phosphorylase
Niemann-Pick disease	sphingomyelinase
phenylketonuria (PKU)	phenylalanine hydroxylase
sickle cell anemia	hemoglobin
Tay-Sachs disease	hexosaminidase A
tyrosinemia	fumarylacetoacetate hydrolase or tyrosine aminotransferase
von Gierke disease	glucose 6-phosphatase
Wilson disease	Wilson disease protein

PKU results from the absence of the enzyme phenylalanine hydroxylase. Without this enzyme, a person cannot convert phenylalanine to tyrosine, which is the precursor of the neurotransmitters dopamine and norepinephrine as well as the skin pigment melanin.



When this reaction cannot occur, phenylalanine accumulates and is then converted to higher than normal quantities of phenylpyruvate. The disease acquired its name from the high levels of phenylpyruvate (a phenyl ketone) in urine. Excessive amounts of phenylpyruvate impair normal brain development, which causes severe mental retardation.



PKU may be diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites. Medical authorities recommend testing every newborn's blood for phenylalanine within 24 h to 3 weeks after birth. If the condition is detected, mental retardation can be prevented by immediately placing the infant on a diet containing little or no phenylalanine. Because phenylalanine is plentiful in naturally produced proteins, the low-phenylalanine diet depends on a synthetic protein substitute plus very small measured amounts of naturally produced foods. Before dietary treatment was introduced in the early 1960s, severe mental retardation was a common outcome for children with PKU. Prior to the 1960s, 85% of patients with PKU had an intelligence quotient (IQ) less than 40, and 37% had IQ scores below 10. Since the introduction of dietary treatments, however, over 95% of children with PKU have developed normal or near-normal intelligence. The incidence of PKU in newborns is about 1 in 12,000 in North America.

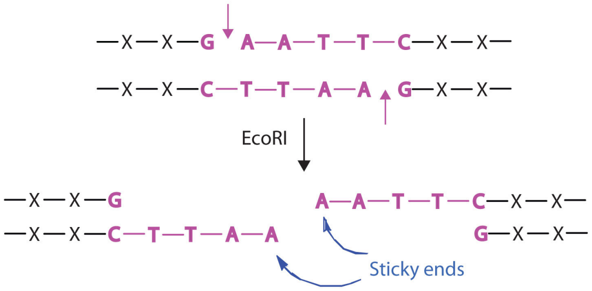
> *Every state in the United States has mandated that screening for PKU be provided to all newborns.*

Several genetic diseases are collectively categorized as *lipid-storage diseases*. Lipids are constantly being synthesized and broken down in the body, so if the enzymes that catalyze lipid degradation are missing, the lipids tend to accumulate and cause a variety of medical problems. When a genetic mutation occurs in the gene for the enzyme hexosaminidase A, for example, gangliosides cannot be degraded but accumulate in brain tissue, causing the ganglion cells of the brain to become greatly enlarged and nonfunctional. This genetic disease, known as *Tay-Sachs disease*, leads to a regression in development, dementia, paralysis, and blindness, with death usually occurring before the age of three. There is currently no treatment, but Tay-Sachs disease can be diagnosed in a fetus by assaying the amniotic fluid (amniocentesis) for hexosaminidase A. A blood test can identify Tay-Sachs carriers—people who inherit a defective gene from only one rather than both parents—because they produce only half the normal amount of hexosaminidase A, although they do not exhibit symptoms of the disease.

Looking Closer: Recombinant DNA Technology

More than 3,000 human diseases have been shown to have a genetic component, caused or in some way modulated by the person's genetic composition. Moreover, in the last decade or so, researchers have succeeded in identifying many of the genes and even mutations that are responsible for specific genetic diseases. Now scientists have found ways of identifying and isolating genes that have specific biological functions and placing those genes in another organism, such as a bacterium, which can be easily grown in culture. With these techniques, known as *recombinant DNA technology*, the ability to cure many serious genetic diseases appears to be within our grasp.

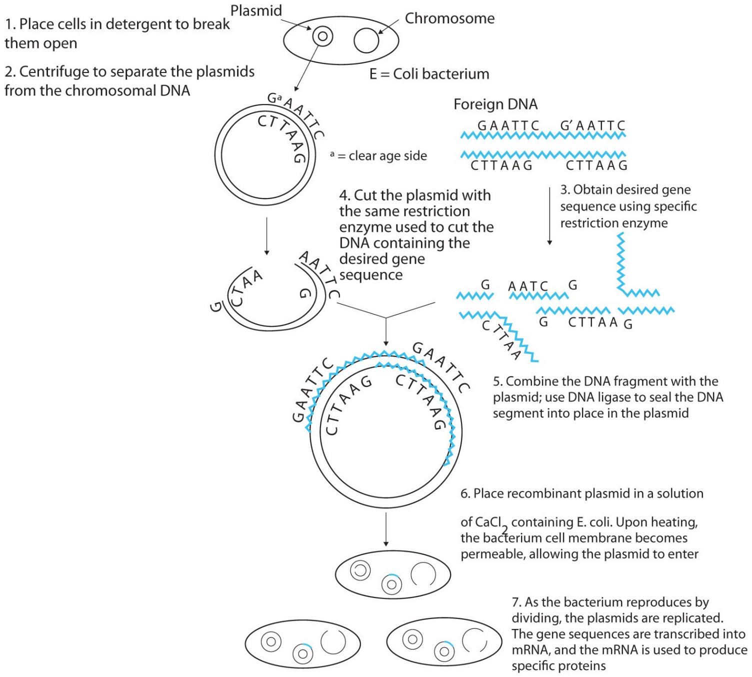
Isolating the specific gene or genes that cause a particular genetic disease is a monumental task. One reason for the difficulty is the enormous amount of a cell's DNA, only a minute portion of which contains the gene sequence. Thus, the first task is to obtain smaller pieces of DNA that can be more easily handled. Fortunately, researchers are able to use *restriction enzymes* (also known as restriction endonucleases), discovered in 1970, which are enzymes that cut DNA at specific, known nucleotide sequences, yielding DNA fragments of shorter length. For example, the restriction enzyme *EcoRI* recognizes the nucleotide sequence shown here and cuts both DNA strands as indicated:



Once a DNA strand has been fragmented, it must be cloned; that is, multiple identical copies of each DNA fragment are produced to make sure there are sufficient amounts of each to detect and manipulate in the laboratory. Cloning is accomplished by inserting the individual DNA fragments into phages (bacterial viruses) that can enter bacterial cells and be replicated. When a bacterial cell infected by the modified phage is placed in an appropriate culture medium, it forms a colony of cells, all containing copies of the original DNA fragment. This technique is used to produce many bacterial colonies, each containing a different DNA fragment. The result is a *DNA library*, a collection of bacterial colonies that together contain the entire genome of a particular organism.

The next task is to screen the DNA library to determine which bacterial colony (or colonies) has incorporated the DNA fragment containing the desired gene. A short piece of DNA, known as a *hybridization probe*, which has a nucleotide sequence complementary to a known sequence in the gene, is synthesized, and a radioactive phosphate group is added to it as a "tag." You might be wondering how researchers are able to prepare such a probe if the gene has not yet been isolated. One way is to use a segment of the desired gene isolated from another organism. An alternative method depends on knowing all or part of the amino acid sequence of the protein produced by the gene of interest: the amino acid sequence is used to produce an approximate genetic code for the gene, and this nucleotide sequence is then produced synthetically. (The amino acid sequence used is carefully chosen to include, if possible, many amino acids such as methionine and tryptophan, which have only a single codon each.)

After a probe identifies a colony containing the desired gene, the DNA fragment is clipped out, again using restriction enzymes, and spliced into another replicating entity, usually a plasmid. *Plasmids* are tiny mini-chromosomes found in many bacteria, such as *Escherichia coli* (*E. coli*). A recombined plasmid would then be inserted into the host organism (usually the bacterium *E. coli*), where it would go to work to produce the desired protein.



Proponents of recombinant DNA research are excited about its great potential benefits. An example is the production of human growth hormone, which is used to treat children who fail to grow properly. Formerly, human growth hormone was available only in tiny amounts obtained from cadavers. Now it is readily available through recombinant DNA technology. Another gene that has been cloned is the gene for epidermal growth factor, which stimulates the growth of skin cells and can be used to speed the healing of burns and other skin wounds. Recombinant techniques are also a powerful research tool, providing enormous aid to scientists as they map and sequence genes and determine the functions of different segments of an organism's DNA.

In addition to advancements in the ongoing treatment of genetic diseases, recombinant DNA technology may actually lead to cures. When appropriate genes are successfully inserted into *E. coli*, the bacteria can become miniature pharmaceutical factories, producing great quantities of insulin for people with diabetes, clotting factor for people with hemophilia, missing enzymes, hormones, vitamins, antibodies, vaccines, and so on. Recent accomplishments include the production in *E. coli* of recombinant DNA molecules containing synthetic genes for tissue plasminogen activator, a clot-dissolving enzyme that can rescue heart attack victims, as well as the production of vaccines against hepatitis B (humans) and hoof-and-mouth disease (cattle).

Scientists have used other bacteria besides *E. coli* in gene-splicing experiments and also yeast and fungi. Plant molecular biologists use a bacterial plasmid to introduce genes for several foreign proteins (including animal proteins) into plants. The bacterium is *Agrobacterium tumefaciens*, which can cause tumors in many plants, but which can be treated so that its tumor-causing ability is eliminated. One practical application of its plasmids would be to enhance a plant's nutritional value by transferring into it the gene necessary for the synthesis of an amino acid in which the plant is normally deficient (for example, transferring the gene for methionine synthesis into pinto beans, which normally do not synthesize high levels of methionine).

> Restriction enzymes have been isolated from a number of bacteria and are named after the bacterium of origin. *EcoRI* is a restriction enzyme obtained from the R strain of *E. coli*. The roman numeral I indicates that it was the first restriction enzyme obtained from this strain of bacteria.

Summary

- The nucleotide sequence in DNA may be modified either spontaneously or from exposure to heat, radiation, or certain chemicals and can lead to mutations.
- Mutagens are the chemical or physical agents that cause mutations.
- Genetic diseases are hereditary diseases that occur because of a mutation in a critical gene.

16.7: Viruses

Learning Objectives

- To explain how viruses reproduce in cells.

Viruses are visible only under an electron microscope. They come in a variety of shapes, ranging from spherical to rod shaped. The fact that they contain either deoxyribonucleic acid (DNA) or ribonucleic acid (RNA)—*but never both*—allows them to be divided into two major classes: DNA viruses and RNA viruses (Figure 16.7.1).

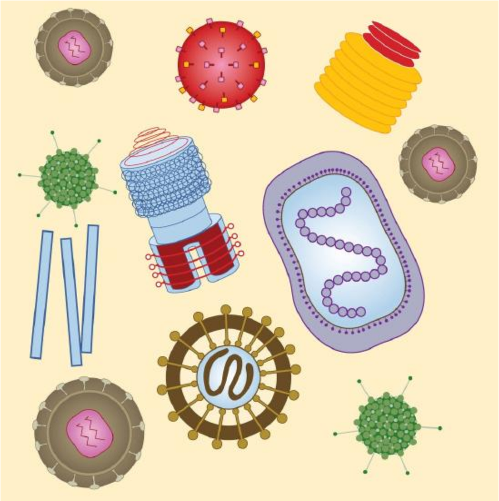


Figure 16.7.1: Viruses. Viruses come in a variety of shapes that are determined by their protein coats.

Most *RNA viruses* use their nucleic acids in much the same way as the DNA viruses, penetrating a host cell and inducing it to replicate the viral RNA and synthesize viral proteins. The new RNA strands and viral proteins are then assembled into new viruses. Some RNA viruses, however, called retroviruses (Figure 16.7.2), synthesize DNA in the host cell, in a process that is the reverse of the DNA-to-RNA transcription that normally occurs in cells. The synthesis of DNA from an RNA template is catalyzed by the enzyme reverse transcriptase.

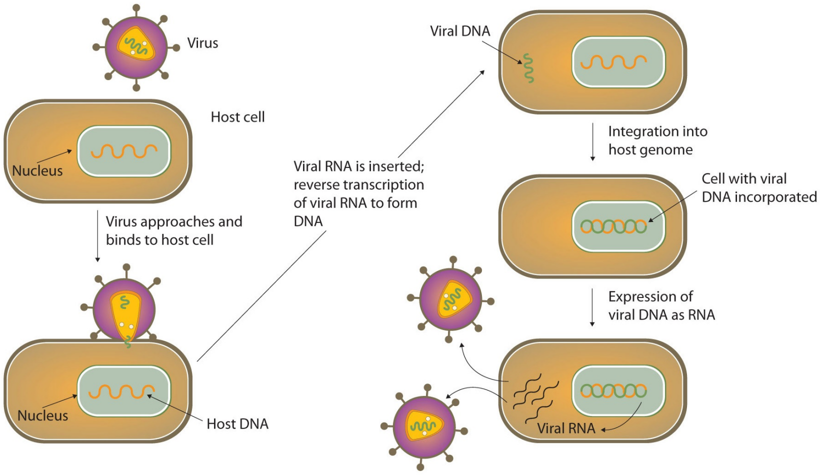
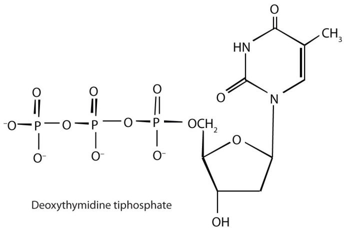
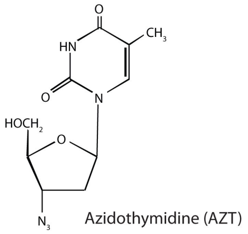


Figure 16.7.2: Life Cycle of a Retrovirus

In 1987, **azidothymidine** (AZT, also known as zidovudine or the brand name Retrovir) became the first drug approved for the treatment of AIDS. It works by binding to reverse transcriptase in place of deoxythymidine triphosphate, after which, because AZT does not have a 3′OH group, further replication is blocked. In the past 10 years, several other drugs have been approved that also act by inhibiting the viral reverse transcriptase.

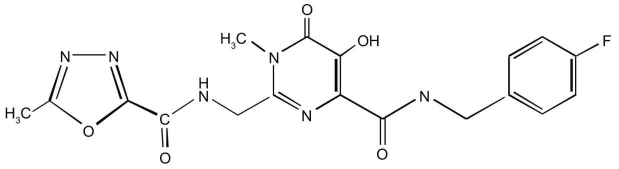


Deoxythymidine tiphosphate



Azidothymidine (AZT)

Raltegravir (Isentress) is a newer anti-AIDS drug that was approved by the FDA in October 2007. This drug inhibits the integrase enzyme that is needed to integrate the HIV DNA into cellular DNA, an essential step in the production of more HIV particles.



Raltegravir

A major problem in treating HIV infections is that the virus can become resistant to any of these drugs. One way to combat the problem has been to administer a “cocktail” of drugs, typically a combination of two reverse transcriptase inhibitors along with a protease inhibitor. These treatments can significantly reduce the amount of HIV in an infected person.

✓ Career Focus: Genetics Counselor

A genetics counselor works with individuals and families who have birth defects or genetic disorders or a family history of a disease, such as cancer, with a genetic link. A genetics counselor may work in a variety of health-care settings (such as a hospital) to obtain family medical and reproductive histories; explain how genetic conditions are inherited; explain the causes, diagnosis, and care of these conditions; interpret the results of genetic tests; and aid the individual or family in making decisions regarding genetic diseases or conditions. A certified genetics counselor must obtain a master’s degree from an accredited program. Applicants to these graduate programs usually have an undergraduate degree in biology, psychology, or genetics.

Photo courtesy of the United States National Institutes for Health, commons.wikimedia.org/wiki/File:Geneticcounseling.jpg.

Summary

Viruses are very small infectious agents that contain either DNA or RNA as their genetic material. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

16.E: Nucleic Acids (Exercises)

19.1: Nucleotides

Concept Review Exercises

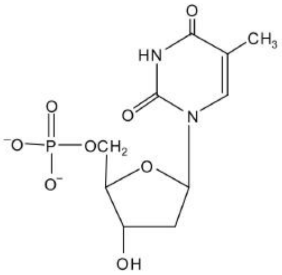
1. Identify the three molecules needed to form the nucleotides in each nucleic acid.
   a. DNA
   b. RNA
2. Classify each compound as a pentose sugar, a purine, or a pyrimidine.
   a. adenine
   b. guanine
   c. deoxyribose
   d. thymine
   e. ribose
   f. cytosine

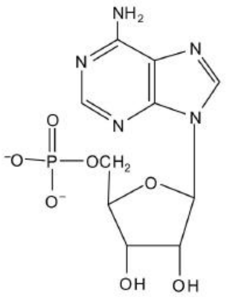
Answers

1. a. nitrogenous base (adenine, guanine, cytosine, and thymine), 2-deoxyribose, and H_3PO_4
   b. nitrogenous base (adenine, guanine, cytosine, and uracil), ribose, and H_3PO_4
2. a. purine
   b. purine
   c. pentose sugar
   d. pyrimidine
   e. pentose sugar
   f. pyrimidine

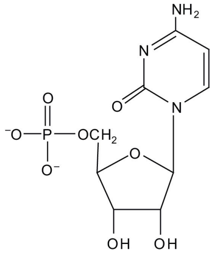
Exercises

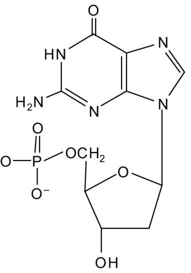
1. What is the sugar unit in each nucleic acid?
   a. RNA
   b. DNA
2. Identify the major nitrogenous bases in each nucleic acid.
   a. DNA
   b. RNA
3. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.
   a.



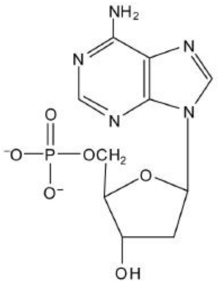
b. 

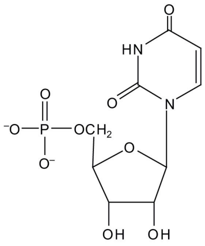
4. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a. 

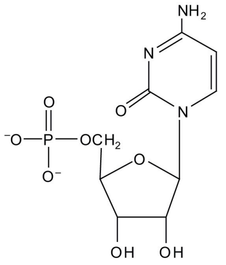
b. 

5. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

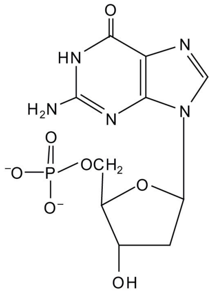
a. 

b. 

6. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.



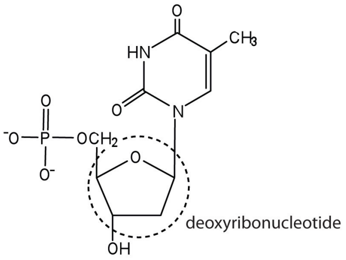
a.



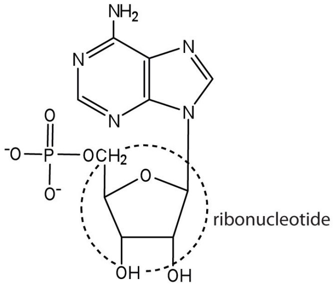
b.

Answers

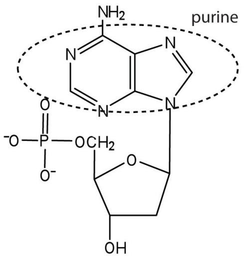
1. a. ribose
   b. deoxyribose



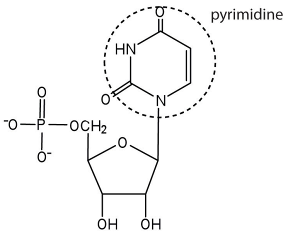
3. a.



b.



a.



b.

19.2: Nucleic Acid Structure

Concept Review Exercises

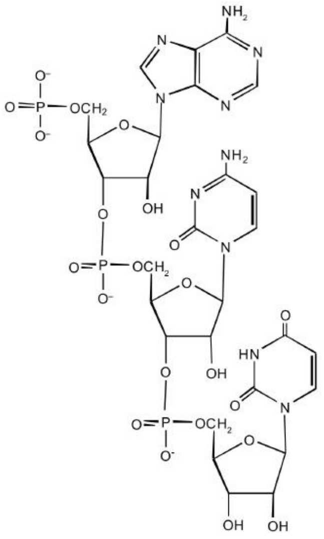
1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

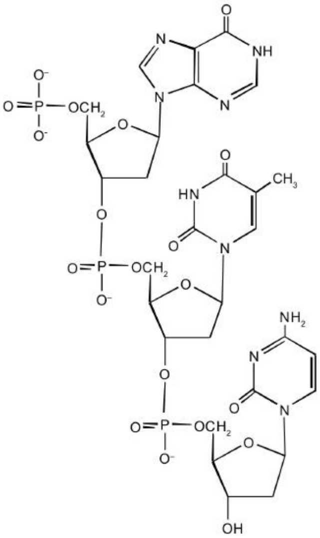
1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.

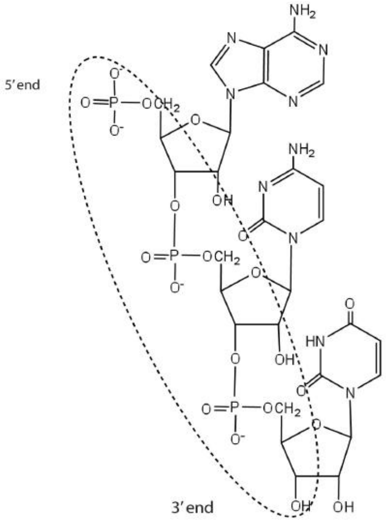


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′
6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers

1. 

    c. ACU

3. a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

19.3: Replication and Expression of Genetic Information

Concept Review Exercises

1. In DNA replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
2. What is the role of DNA in transcription? What is produced in transcription?
3. Which type of RNA contains the codon? Which type of RNA contains the anticodon?

Answers

1. Each strand of the parent DNA double helix remains associated with the newly synthesized DNA strand.
2. DNA serves as a template for the synthesis of an RNA strand (the product of transcription).
3. codon: mRNA; anticodon: tRNA

Exercises

1. Describe how replication and transcription are similar.
2. Describe how replication and transcription differ.
3. A portion of the coding strand for a given gene has the sequence 5′-ATGAGCGACTTTGCGGGATTA-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?
4. A portion of the coding strand for a given gene has the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Answers

1. Both processes require a template from which a complementary strand is synthesized.

3.

a. 3′-TACTCGCTGAAACGCCCTAAT-5′
b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

19.4: Protein Synthesis and the Genetic Code

Concept Review Exercises

1. What are the roles of mRNA and tRNA in protein synthesis?
2. What is the initiation codon?
3. What are the termination codons and how are they recognized?

Answers

1. mRNA provides the code that determines the order of amino acids in the protein; tRNA transports the amino acids to the ribosome to incorporate into the growing protein chain.
2. AUG
3. UAA, UAG, and UGA; they are recognized by special proteins called release factors, which signal the end of the translation process.

Exercises

1. Write the anticodon on tRNA that would pair with each mRNA codon.
    a. 5′-UUU-3′
    b. 5′-CAU-3′
    c. 5′-AGC-3′
    d. 5′-CCG-3′
2. Write the codon on mRNA that would pair with each tRNA anticodon.
    a. 5′-UUG-3′
    b. 5′-GAA-3′
    c. 5′-UCC-3′
    d. 5′-CAC-3′
3. The peptide hormone oxytocin contains 9 amino acid units. What is the minimum number of nucleotides needed to code for this peptide?
4. Myoglobin, a protein that stores oxygen in muscle cells, has been purified from a number of organisms. The protein from a sperm whale is composed of 153 amino acid units. What is the minimum number of nucleotides that must be present in the mRNA that codes for this protein?
5. Use Figure $16.E.3$ to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure $16.E.3$ to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure $16.E.3$ to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure $16.E.3$ to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGGCAAUCCUCAAACGCUGU-3′

Answers

1. a. 3′-AAA-5′
    b. 3′-GUA-5′
    c. 3′-UCG-5′
    d. 3′-GGC-5′

3. 27 nucleotides (3 nucleotides/codon)

5. 1a: phenylalanine; 1b: histidine; 1c: serine; 1d: proline

7. met-ser-asp-phe-ala-gly-leu

19.5: Mutations and Genetic Diseases

Concept Review Exercises

1. a. What effect can UV radiation have on DNA?
    b. Is UV radiation an example of a physical mutagen or a chemical mutagen?

2. a. What causes PKU?
    b. How is PKU detected and treated?

Answers

1. a. It can lead to the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer.
    b. physical mutagen

2. a. the absence of the enzyme phenylalanine hydroxylase
    b. PKU is diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites; treatment calls for an individual to be placed on a diet containing little or no phenylalanine.

Exercises

1. A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGAGCGACCTTCGCCCATTA-3′.

   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
2. A portion of the coding strand of a gene was found to have the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′. A mutation occurred in the gene, making the sequence 5′-ATGGCAATCCTCAACGCTGT-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
3. a. What is a mutagen?
   b. Give two examples of mutagens.
4. For each genetic disease, indicate which enzyme is lacking or defective and the characteristic symptoms of the disease.
   a. PKU
   b. Tay-Sachs disease

Answers

1. a. substitution
   b. Phenylalanine (UUU) would be replaced with leucine (CUU).
3. a. a chemical or physical agent that can cause a mutation
   b. UV radiation and gamma radiation (answers will vary)

19.6: Viruses

Questions

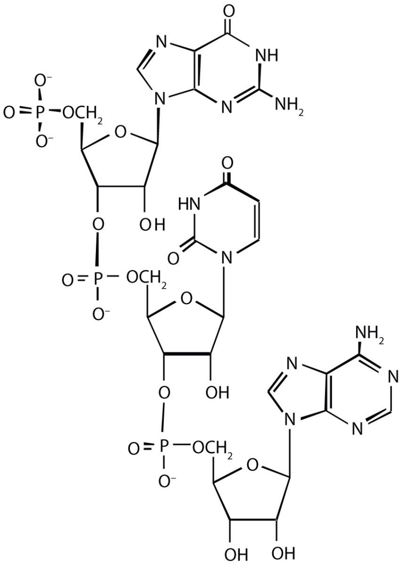
1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5. a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. What HIV enzyme does AZT inhibit?
7. What HIV enzyme does raltegravir inhibit?

Answers

1. A virus consists of a central core of nucleic acid enclosed in a protective shell of proteins. There may be lipid or carbohydrate molecules on the surface.
2. A DNA virus has DNA as its genetic material, while an RNA virus has RNA as its genetic material.
3. In a cell, a retrovirus synthesizes a DNA copy of its RNA genetic material.
4. The DNA virus enters a host cell and induces the cell to replicate the viral DNA and produce viral proteins. These proteins and DNA assemble into new viruses that are released by the host cell, which may die in the process.
5. -
6. reverse transcriptase
7. -

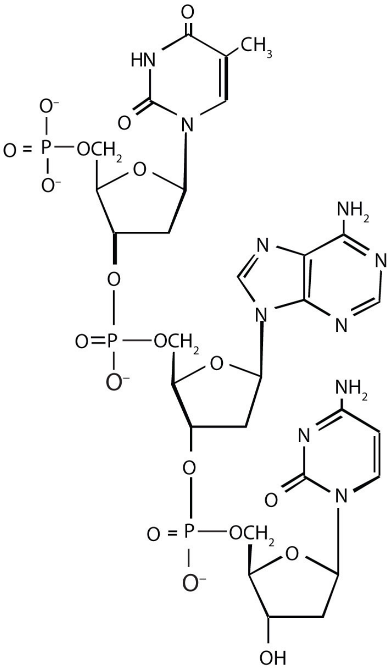
Additional Exercises

1. For this nucleic acid segment,



a. classify this segment as RNA or DNA and justify your choice.
b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

2. For this nucleic acid segment,



a. classify this segment as RNA or DNA and justify your choice.
b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

3. One of the key pieces of information that Watson and Crick used in determining the secondary structure of DNA came from experiments done by E. Chargaff, in which he studied the nucleotide composition of DNA from many different species. Chargaff noted that the molar quantity of A was always approximately equal to the molar quantity of T, and the molar quantity of C was always approximately equal to the molar quantity of G. How were Chargaff's results explained by the structural model of DNA proposed by Watson and Crick?

4. Suppose Chargaff (see Exercise 3) had used RNA instead of DNA. Would his results have been the same; that is, would the molar quantity of A approximately equal the molar quantity of T? Explain.

5. In the DNA segment

5′-ATGAGGCATGAGACG-3′ (coding strand) 3′-TACTCCGTACTCTGC-5′ (template strand)

   a. What products would be formed from the segment’s replication?
   b. Write the mRNA sequence that would be obtained from the segment’s transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 5b?

6. In the DNA segment

   5′-ATGACGGTTTACTAAGCC-3′ (coding strand) 3′-TACTGCCAAATGATTCGG-5′ (template strand)

   a. What products would be formed from the segment’s replication?
   b. Write the mRNA sequence that would be obtained from the segment’s transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 6b?

7. A hypothetical protein has a molar mass of 23,300 Da. Assume that the average molar mass of an amino acid is 120.

   a. How many amino acids are present in this hypothetical protein?
   b. What is the minimum number of codons present in the mRNA that codes for this protein?
   c. What is the minimum number of nucleotides needed to code for this protein?

8. Bradykinin is a potent peptide hormone composed of nine amino acids that lowers blood pressure.

   a. The amino acid sequence for bradykinin is arg-pro-pro-gly-phe-ser-pro-phe-arg. Postulate a base sequence in the mRNA that would direct the synthesis of this hormone. Include an initiation codon and a termination codon.
   b. What is the nucleotide sequence of the DNA that codes for this mRNA?

9. A particular DNA coding segment is ACGTTAGCCCCAGCT.

   a. Write the sequence of nucleotides in the corresponding mRNA.
   b. Determine the amino acid sequence formed from the mRNA in Exercise 9a during translation.
   c. What amino acid sequence results from each of the following mutations?
      a. replacement of the underlined guanine by adenine
      b. insertion of thymine immediately after the underlined guanine
      c. deletion of the underlined guanine

10. A particular DNA coding segment is TACGACGTAACAAGC.

    a. Write the sequence of nucleotides in the corresponding mRNA.
    b. Determine the amino acid sequence formed from the mRNA in Exercise 10a during translation.
    c. What amino acid sequence results from each of the following mutations?
       a. replacement of the underlined guanine by adenine
       b. replacement of the underlined adenine by thymine

11. Two possible point mutations are the substitution of lysine for leucine *or* the substitution of serine for threonine. Which is likely to be more serious and why?
12. Two possible point mutations are the substitution of valine for leucine *or* the substitution of glutamic acid for histidine. Which is likely to be more serious and why?

Answers

1.
   a. RNA; the sugar is ribose, rather than deoxyribose
   b. 5′-GUA-3′

3. In the DNA structure, because guanine (G) is always paired with cytosine (C) and adenine (A) is always paired with thymine (T), you would expect to have equal amounts of each.

5.

a. Each strand would be replicated, resulting in two double-stranded segments.
b. 5′-AUGAGGCAUGAGACG-3′
c. met-arg-his-glu-thr

7.

a. 194
b. 194
c. 582

9.

a. 5′-ACGUUAGCCCCAGCU-3′
b. thr-leu-ala-pro-ala
c.
    a. thr-leu-thr-pro-ala
    b. thr-leu-val-pro-ser
    c. thr-leu-pro-gin

11. substitution of lysine for leucine because you are changing from an amino acid with a nonpolar side chain to one that has a positively charged side chain; both serine and threonine, on the other hand, have polar side chains containing the OH group.

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16.S: Nucleic Acids (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A cell's hereditary information is encoded in **chromosomes** in the cell's nucleus. Each chromosome is composed of proteins and **deoxyribonucleic acid (DNA)**. The chromosomes contain smaller hereditary units called **genes,** which are relatively short segments of DNA. The hereditary information is expressed or used through the synthesis of **ribonucleic acid (RNA)**. Both **nucleic acids**—DNA and RNA—are polymers composed of monomers known as **nucleotides**, which in turn consist of phosphoric acid (H_3PO_4), a nitrogenous base, and a pentose sugar.

The two types of *nitrogenous bases* most important in nucleic acids are **purines**—adenine (A) and guanine (G)—and **pyrimidines**—cytosine (C), thymine (T), and uracil (U). DNA contains the nitrogenous bases adenine, cytosine, guanine, and thymine, while the bases in RNA are adenine, cytosine, guanine, and uracil. The sugar in the nucleotides of RNA is ribose; the one in DNA is 2-deoxyribose. The sequence of nucleotides in a nucleic acid defines the primary structure of the molecule.

RNA is a single-chain nucleic acid, whereas DNA possesses two nucleic-acid chains intertwined in a secondary structure called a **double helix**. The sugar-phosphate backbone forms the outside the double helix, with the purine and pyrimidine bases tucked inside. Hydrogen bonding between **complementary bases** holds the two strands of the double helix together; A always pairs with T and C always pairs with G.

Cell growth requires **replication**, or reproduction of the cell's DNA. The double helix unwinds, and hydrogen bonding between complementary bases breaks so that there are two single strands of DNA, and each strand is a *template* for the synthesis of a new strand. For protein synthesis, three types of RNA are needed: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). All are made from a DNA template by a process called **transcription**. The double helix uncoils, and ribonucleotides base-pair to the deoxyribonucleotides on one DNA strand; however, RNA is produced using *uracil* rather than thymine. Once the RNA is formed, it dissociates from the template and leaves the nucleus, and the DNA double helix reforms.

Translation is the process in which proteins are synthesized from the information in mRNA. It occurs at structures called **ribosomes**, which are located outside the nucleus and are composed of rRNA and protein. The 64 possible three-nucleotide combinations of the 4 nucleotides of DNA constitute the **genetic code** that dictates the sequence in which amino acids are joined to make proteins. Each three-nucleotide sequence on mRNA is a **codon**. Each kind of tRNA molecule binds a specific amino acid and has a site containing a three-nucleotide sequence called an **anticodon**.

The general term for any change in the genetic code in an organism's DNA is **mutation**. A change in which a single base is substituted, inserted, or deleted is a **point mutation**. The chemical and/or physical agents that cause mutations are called **mutagens**. Diseases that occur due to mutations in critical DNA sequences are referred to as **genetic diseases**.

Viruses are infectious agents composed of a tightly packed central core of nucleic acids enclosed by a protective shell of proteins. Viruses contain either DNA or RNA as their genetic material but not both. Some RNA viruses, called **retroviruses**, synthesize DNA in the host cell from their RNA genome. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

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