

UWX CH114: CHEMISTRY IN THE KITCHEN



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UWX CH114 - Chemistry in the Kitchen

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CHAPTER OVERVIEW

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1.1: The Elements

Learning Objectives

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

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure 1.1.1 shows some of the chemical elements.



Figure 1.1.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Abundance

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

Table 1.1.1: Elemental Composition of Earth

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

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

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

the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table 1.1.1 lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table 1.1.2 lists the relative abundances of elements in the human body. If you compare Table 1.1.1 and Table 1.1.2, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 1.1.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table 1.1.2: Elemental Composition of a Human Body

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

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

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

📌 LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

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

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

Names and Symbols

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

Today, new elements are usually named after famous scientists.

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 1.1.3 lists the names and symbols of some of the most familiar elements.

Table 1.1.3: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

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

lithium	Li	zirconium	Zr
*The symbol comes from the Latin name of element.			
†The symbol for tungsten comes from its German name— <i>wolfram</i> .			

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

✓ Example 1.1.1

Write the chemical symbol for each element without consulting Table 1.1.3 "Element Names and Symbols".

- bromine
- boron
- carbon
- calcium
- gold

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

? Exercise 1.1.1

Write the chemical symbol for each element without consulting Table 1.1.3.

- manganese
- magnesium
- neon
- nitrogen
- silver

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

✓ **Example 1.1.2**

What element is represented by each chemical symbol?

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

Answer a

sodium

Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

? **Exercise 1.1.2**

What element is represented by each chemical symbol?

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

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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1.1.1: What is Chemistry?

Learning Objectives

1. Define chemistry in relation to other sciences.
2. Identify the general steps in the scientific method.

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

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure 1.1.1.1). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

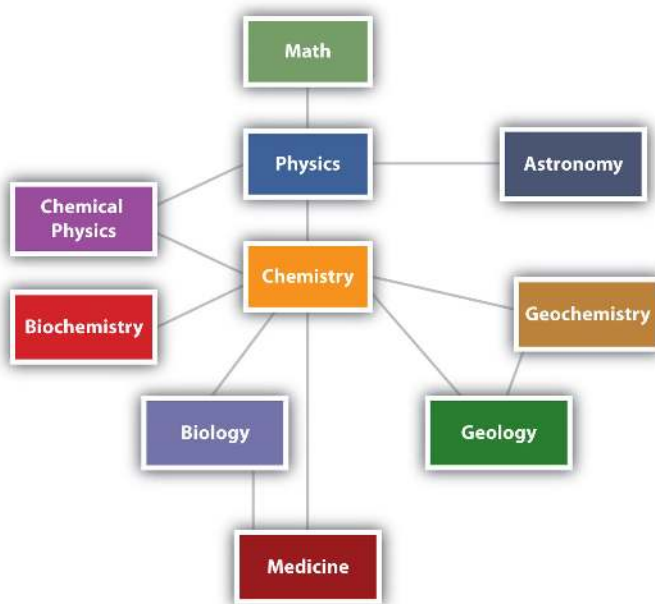


Figure 1.1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure 1.1.1.1 shows how many of the individual fields of science are related.

There are many other fields of science in addition to the ones listed here.

Alchemy

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

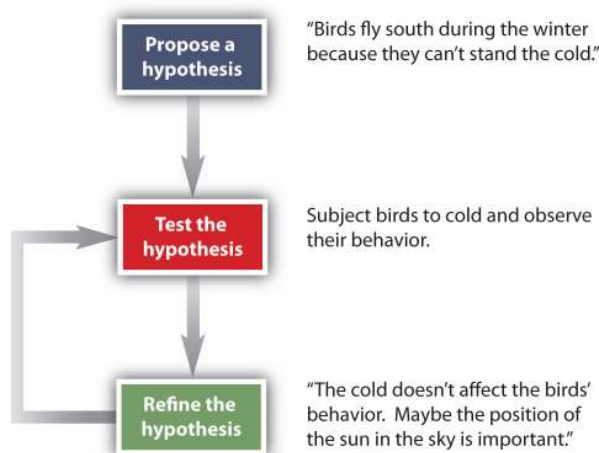
Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Practitioners, called alchemists, thought that all matter was composed of different proportions of the four basic elements—fire, water, earth, and air—and believed that if you changed the relative proportions of these elements in a substance, you could change the substance. The long-standing attempts to “transmute” common metals into gold represented one goal of alchemy. Alchemy’s other major goal was to synthesize the philosopher’s stone, a material that could impart long life—even immortality. Alchemists used

[illegible]

Esprits acides.	Terre absorbante.	Q Cuivre.	♂ Soufre minéral. [Principe.
Acide du sel marin.	^{SN} Substances métalliques.	♂ Fer.	♂ Principe huileux ou Soufre
Acide nitreux.	☿ Mercure.	♂ Plomb.	♂ Esprit de vinaigre.
Acide vitriolique.	♂ Règle d'Antimoine.	♂ Etain.	▽ Eau.
Sel alcali fixe.	♂ Or.	♂ Zinc.	⊖ Sel
Sel alcali volatil.	♂ Argent.	♂ Pierre Calaminaire.	▽ Esprit de vin et Esprits ar-

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

Generally, they follow a process called the scientific method. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. To find the answer to a question (for example, “Why do birds fly toward Earth’s equator during the cold months?”), a scientist goes through the following steps, which are also illustrated in Figure 1.1.1.2



The steps may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

1. **Propose a hypothesis.** A scientist generates a testable idea, or hypothesis, to try to answer a question or explain an observation about how the natural universe works. Some people use the word *theory* in place of hypothesis, but the word hypothesis is the proper word in science. For scientific applications, the word theory is a general statement that describes a large set of observations and data. A theory represents the highest level of scientific understanding.
2. **Test the hypothesis.** A scientist evaluates the hypothesis by devising and carrying out experiments to test it. If the hypothesis passes the test, it may be a proper answer to the question. If the hypothesis does not pass the test, it may not be a good answer.
3. **Refine the hypothesis if necessary.** Depending on the results of experiments, a scientist may want to modify the hypothesis and then test it again. Sometimes the results show the original hypothesis to be completely wrong, in which case a scientist will have to devise a new hypothesis.

Not all scientific investigations are simple enough to be separated into these three discrete steps. But these steps represent the general method by which scientists learn about our natural universe.



Key Takeaways

- Chemistry is the study of matter and how it behaves.
- The scientific method is the general process by which we learn about the natural universe.

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1.1.2: Measurements

Learning Objectives

- Express quantities properly using a number and a unit.

A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 1.1.2.1); the nurse is also measuring.



Figure 1.1.2.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GNU Free Documentation License; Pia von Lützau via Wikipedia).

Chemists measure the properties of matter using a variety of devices or measuring tools, many of which are similar to those used in everyday life. Rulers are used to measure length, balances (scales) are used to measure mass (weight), and graduated cylinders or pipettes are used to measure volume. Measurements made using these devices are expressed as quantities. A **quantity** is an amount of something and consists of a **number** and a **unit**. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5.2 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5.2.

5.2 kilometers
number unit

If you ask a friend how far he or she walks from home to school, and the friend answers "12" without specifying a unit, you do not know whether your friend walks—for example, 12 miles, 12 kilometers, 12 furlongs, or 12 yards.

Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

Both a number and a unit must be included to express a quantity properly.

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

✓ Exercise 1.1.2.1

Identify the **number** and the **unit** in each quantity.

- one dozen eggs
- 2.54 centimeters
- a box of pencils
- 88 meters per second

Answer a

The number is one, and the unit is dozen.

Answer b

The number is 2.54, and the unit is centimeter.

Answer c

The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.

Answer d

The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.

? Exercise 1.1.2.2

Identify the **number** and the **unit** in each quantity.

- a. 99 bottles of soda
- b. 60 miles per hour
- c. 32 fluid ounces
- d. 98.6 degrees Fahrenheit

Answer a

The number is 99, and the unit is bottles of soda.

Answer b

The number is 60, and the unit is miles per hour.

Answer c

The number 32, and the unit is fluid ounces

Answer d

The number is 98.6, and the unit is degrees Fahrenheit

? Exercise 1.1.2.2

What are the two necessary parts of a quantity?

Answer

The two necessary parts are the number and the unit.

Key Takeaway

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

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1.2: Atomic Theory

Learning Objectives

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.
- Recognize which elements exist as diatomic molecules.

Take some aluminum foil. Cut it in half. Now you have two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil.

It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can you take this exercise, at least in theory? Can you continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? (Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC.)

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 1.2.1), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

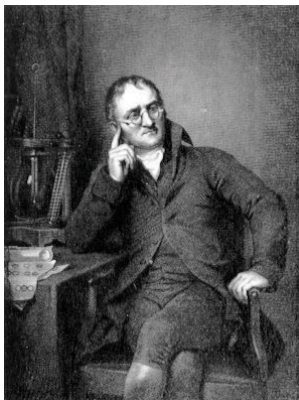


Figure 1.2.1 John Dalton was an English scientist who enunciated the modern atomic theory.

Most elements in their pure form exist as **individual atoms**. For example, a macroscopic chunk of iron (Fe) metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called **diatomic molecules**. In representing a diatomic molecule, we use the symbol of the element and include the **subscript** "2" to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H₂), nitrogen (N₂), fluorine (F₂), oxygen (O₂), iodine (I₂), chlorine (Cl₂) and bromine (Br₂). A few other elements can exist as 3-atom molecules like ozone (O₃) and 4-atom molecules like phosphorus (P₄). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S₈ (Figure 1.2.2).

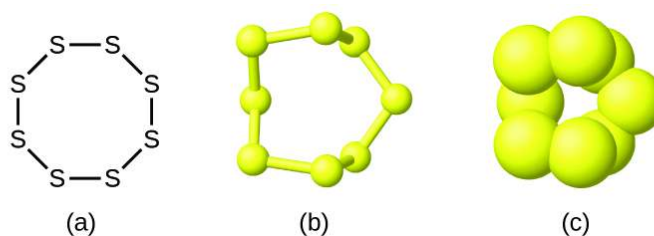


Figure 1.2.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8 . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and $2H$ represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression $2H$, on the other hand, indicates two separate hydrogen atoms that are **not** combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 1.2.3).

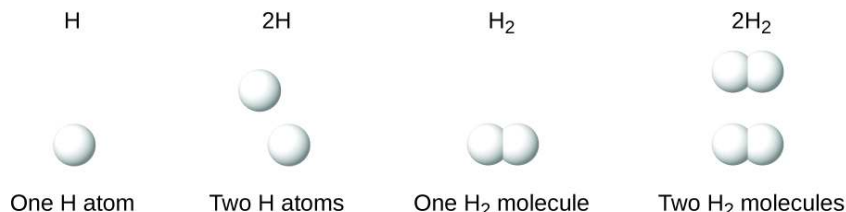


Figure 1.2.3: The symbols H , $2H$, H_2 , and $2H_2$ represent very different entities.

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for $2H$ shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H_2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for $2H_2$ shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

✓ Example 1.2.1

Write the chemical formula of the following elements:

- oxygen
- carbon
- potassium

Solution

Memorizing the diatomic molecules is worthwhile for our future endeavors. A mnemonic device to help in the memorization of the diatomic elements is as follows: **Have No Fear Of Ice Cold Beer**. (hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine).

- Oxygen is one of the seven diatomic molecular elements. Its chemical formula is O_2 .
- Carbon is monatomic, hence its formula is C.
- Potassium is monatomic hence its formula is K.

Exercise

Write the chemical formula of the following elements:

- hydrogen
- nitrogen
- neon

Answer a

Hydrogen is one of the seven diatomic molecular elements. Its chemical formula is H_2 .

Answer b

Nitrogen is one of the seven diatomic molecular elements. Its chemical formula is N_2 .

Answer c

Neon is a monatomic element, hence its formula is Ne.

Looking Closer: Atomic Theory

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means “indivisible” or “uncuttable.”) Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. So when Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Concept Review Exercises

1. What is the modern atomic theory?
2. What are atoms?

Answers

1. The modern atomic theory states that all matter is composed of atoms.
2. Atoms are the smallest parts of an element that maintain the identity of that element.

Key Takeaways

- **Atoms** are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of **atoms** and how they compose matter.
- The **diatomic** elements are hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine.

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1.3: The Structure of Atoms

Learning Objectives

- Describe the three main subatomic particles.
- State how the subatomic particles are arranged in atoms.

There have been several minor but important modifications to Dalton's atomic theory. For one thing, Dalton considered atoms to be indivisible. We know now that atoms not only can be divided but also are composed of three different kinds of particle, *subatomic particles*, with their own properties that are different from the chemical properties of atoms.

Subatomic Particles

The first subatomic particle was identified in 1897 and called the electron. It is an extremely tiny particle, with a mass of about 9.109×10^{-31} kg. Experiments with magnetic fields showed that the electron has a negative electrical charge. By 1920, experimental evidence indicated the existence of a second particle. A proton has the same amount of charge as an electron, but its charge is positive, not negative. Another major difference between a proton and an electron is mass. Although still incredibly small, the mass of a proton is 1.673×10^{-27} kg, which is almost 2,000 times greater than the mass of an electron. Because opposite charges attract each other (while like charges repel each other), protons attract electrons (and vice versa).

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table 1.3.1 lists some of their important characteristics and the symbols used to represent each particle.

Table 1.3.1: Properties of the Subatomic Particles

Particle	Symbol	Mass (kg)	Relative Mass (proton = 1)	Relative Charge
proton	p^+	1.673×10^{-27}	1	+1
neutron	n^0	1.675×10^{-27}	1	0
electron	e^-	9.109×10^{-31}	0.00055	-1

The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure 1.3.1 shows a diagram of the experimental setup.

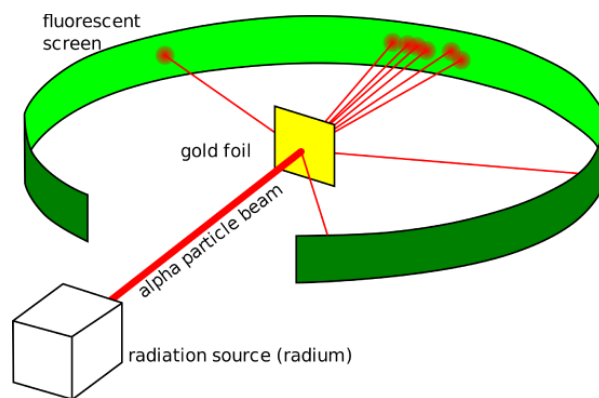


Figure 1.3.1: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, “It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.” (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom’s size. As a result, an atom consists largely of empty space. Rutherford called his description the “planetary model” of the atom. Figure 1.3.2 shows how this model explains the experimental results.

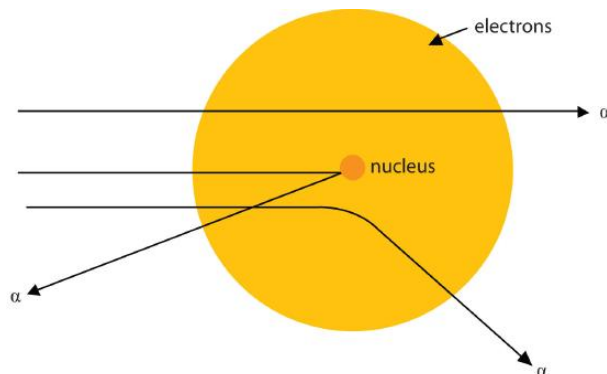


Figure 1.3.2: Rutherford’s Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

The planetary model of the atom replaced the plum pudding model, which had electrons floating around aimlessly like plums in a “pudding” of positive charge.

Rutherford’s model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure 1.3.3 shows a more modern version of our understanding of atomic structure.

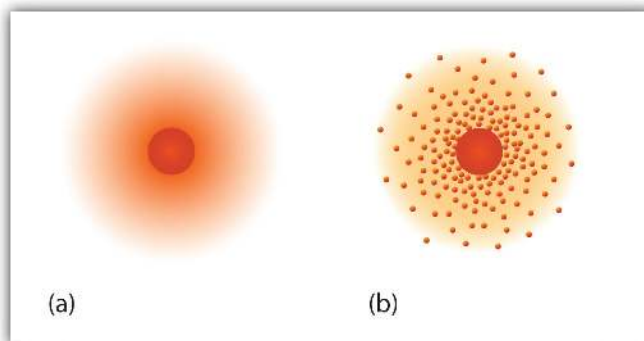


Figure 1.3.3: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

Concept Review Exercises

1. What are the charges and the relative masses of the three subatomic particles?
2. Describe the structure of an atom in terms of its protons, neutrons, and electrons.

Answers

1. proton: +1, large; neutron: 0, large; electron: -1, small
2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

Key Takeaways

- Atoms are composed of three main subatomic particles: protons, neutrons, and electrons.
- Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

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1.4: Nuclei of Atoms

Learning Objectives

- Define and differentiate between the atomic number and the mass number of an element.
- Explain how isotopes differ from one another.

Now that we know how atoms are generally constructed, what do atoms of any particular element look like? How many protons, neutrons, and electrons are in a specific kind of atom? First, if an atom is electrically neutral overall, then the number of protons equals the number of electrons. Because these particles have the same but opposite charges, equal numbers cancel out, producing a neutral atom.

Atomic Number

In the 1910s, experiments with x-rays led to this useful conclusion: the magnitude of the positive charge in the nucleus of every atom of a particular element is the same. In other words, all atoms of the same element have the same number of protons. Furthermore, different elements have a different number of protons in their nuclei, so the number of protons in the nucleus of an atom is characteristic of a particular element. This discovery was so important to our understanding of atoms that the number of protons in the nucleus of an atom is called the atomic number (Z).

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table 1.4.1 lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

Table 1.4.1: Some Common Elements and Their Atomic Numbers

Element	Atomic Number	Element	Atomic Number
aluminum (Al)	13	magnesium (Mg)	12
americium (Am)	95	manganese (Mn)	25
argon (Ar)	18	mercury (Hg)	80
barium (Ba)	56	neon (Ne)	10
beryllium (Be)	4	nickel (Ni)	28
bromine (Br)	35	nitrogen (N)	7
calcium (Ca)	20	oxygen (O)	8
carbon (C)	6	phosphorus (P)	15
chlorine (Cl)	17	platinum (Pt)	78
chromium (Cr)	24	potassium (K)	19
cesium (Cs)	55	radon (Rn)	86
fluorine (F)	9	silver (Ag)	47
gallium (Ga)	31	sodium (Na)	11
gold (Au)	79	strontium (Sr)	38
helium (He)	2	sulfur (S)	16
hydrogen (H)	1	titanium (Ti)	22
iron (Fe)	26	tungsten (W)	74

Element	Atomic Number	Element	Atomic Number
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

✓ Example 1.4.1

What is the number of protons in the nucleus of each element?

- a. aluminum
- b. iron
- c. carbon

Answer a

According to Table 2.4.1, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.

Answer b

Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.

Answer c

Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.

? Exercise 1.4.1

What is the number of protons in the nucleus of each element? Use Table 2.4.1.

- a. sodium
- b. oxygen
- c. chlorine

Answer a

Sodium has 11 protons in its nucleus.

Answer b

Oxygen has 8 protons in its nucleus.

Answer c

Chlorine has 17 protons in its nucleus

How many electrons are in an atom? Previously we said that for an electrically neutral atom, the **number of electrons equals the number of protons**, so the total opposite charges cancel. Thus, the **atomic number** of an element also gives the **number of electrons** in an atom of that element. (Later we will find that some elements may gain or lose electrons from their atoms, so those atoms will no longer be electrically neutral. Thus we will need a way to differentiate the number of electrons for those elements.)

✓ Example 1.4.2

How many electrons are present in the atoms of each element?

- a. sulfur
- b. tungsten
- c. argon

Answer a

The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.

Answer b

The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.

Answer c

The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

? Exercise 1.4.2

How many electrons are present in the atoms of each element?

- a. magnesium
- b. potassium
- c. iodine

Answer a

Mg has 12 electrons.

Answer b

K has 19 electrons.

Answer c

I has 53 electrons.

Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number (Z)**. Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number (A)**, which is the **sum of the numbers of protons and neutrons**.

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 1.4.2.

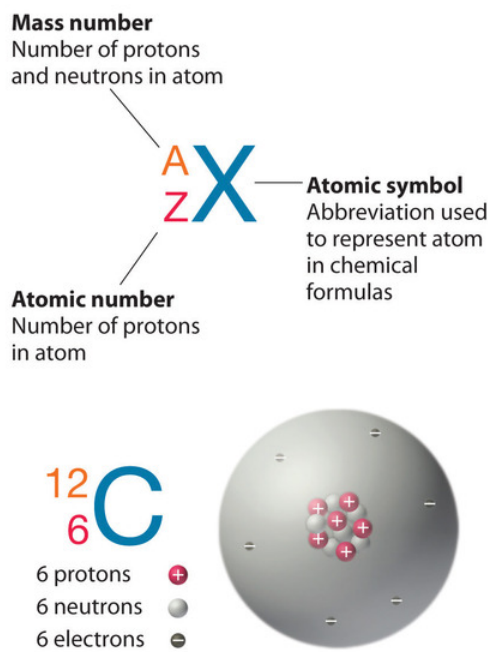


Figure 1.4.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

The atomic symbol, X, is the abbreviation used to represent an atom in chemical formulas. The mass number, A, is the number of protons and neutrons in the atom, which is to the left of the X. The atomic number, Z, is the number of protons in the atom, which is to the left of the X and below the A.

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. What is the mass number of an element?

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. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.

Key Takeaways

- Each element is identified by its atomic number. The atomic number provides the element's location on the periodic table
- The isotopes of an element have different masses and are identified by their mass numbers.

Optional Reading: Isotopes are Elements with Varying Numbers of Neutrons

How many neutrons are in atoms of a particular element? At first it was thought that the number of neutrons in a nucleus was also characteristic of an element. However, it was found that atoms of the same element can have *different* numbers of neutrons. Atoms of the same element (i.e., same atomic number, Z) that have different numbers of neutrons are called isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei; about 1% of the carbon atoms have 7 neutrons in their nuclei. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon with 6 neutrons in each nucleus.

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 1.4.1 compares the three isotopes of hydrogen.

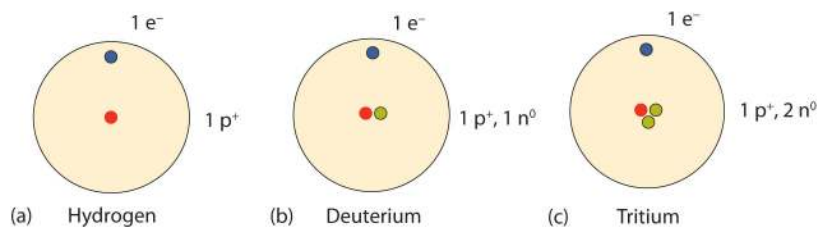


Figure 1.4.1: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

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.

Most elements exist as mixtures of isotopes. In fact, 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. The *mass number* (A) of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

A simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol. Thus, we might see



which indicates a particular isotope of iron. The 26 is the atomic number (which is the same for all iron atoms), while the 56 is the mass number of the isotope. To determine the number of neutrons in this isotope, we subtract 26 from 56: $56 - 26 = 30$, so there are 30 neutrons in this atom.

✓ Example 1.4.3

How many protons and neutrons are in each atom?

- ${}^{35}_{17}\text{Cl}$
- ${}^{127}_{53}\text{I}$

Answer a

In ${}^{35}_{17}\text{Cl}$ there are 17 protons, and $35 - 17 = 18$ neutrons in each nucleus.

Answer b

In ${}^{127}_{53}\text{I}$ there are 53 protons, and $127 - 53 = 74$ neutrons in each nucleus.

? Exercise 1.4.3

How many protons and neutrons are in each atom?

- ${}^{197}_{79}\text{Au}$
- ${}^{23}_{11}\text{Na}$

Answer a

In ${}^{197}_{79}\text{Au}$ there are 79 protons, and $197 - 79 = 118$ neutrons in each nucleus.

Answer b

In ${}^{23}_{11}\text{Na}$ there are 11 protons, and $23 - 11 = 12$ neutrons in each nucleus.

It is not absolutely necessary to indicate the atomic number as a subscript because each element has its own unique atomic number. Many isotopes are indicated with a superscript only, such as ^{13}C or ^{235}U . You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

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1.5: Atomic Masses

Learning Objectives

- Define atomic mass and atomic mass unit.
- Calculate atomic mass.

Even though atoms are very tiny pieces of matter, they have mass. Their masses are so small, however, that chemists often use a unit other than grams to express them—the atomic mass unit.

Atomic Mass Unit and Reported Atomic Mass of the Elements

The atomic mass unit (abbreviated u, although amu is also used) is defined as 1/12 of the mass of a ^{12}C atom:

$$1 \text{ u} = \frac{1}{12} \text{ the mass of } ^{12}\text{C} \text{ atom} \quad (1.5.1)$$

It is equal to 1.661×10^{-24} g.

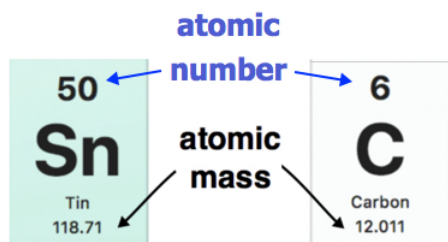
By calculating an average of an element's atomic masses, weighted by the natural abundance of each isotope, we obtain a weighted average mass called the atomic mass (also commonly referred to as the *atomic weight*) of an element.

Most elements occur naturally as a mixture of two or more isotopes - atoms with a variable number of neutrons. Listed below are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table 1.5.1: Atomic Masses and Percent Abundances of Some Natural Isotopes

Element	Isotope (Symbol)	Percent Natural Abundance	Atomic Mass (amu)	Average Atomic Mass (amu)
Hydrogen	^1_1H	99.985	1.0078	1.0079
	^2_1H	0.015	2.0141	
	^3_1H	negligible	3.0160	
Carbon	$^{12}_6\text{C}$	98.89	12.000	12.011
	$^{13}_6\text{C}$	1.11	13.003	
	$^{14}_6\text{C}$	trace	14.003	
Oxygen	$^{16}_8\text{O}$	99.759	15.995	15.999
	$^{17}_8\text{O}$	0.037	16.995	
	$^{18}_8\text{O}$	0.204	17.999	
Chlorine	$^{35}_{17}\text{Cl}$	75.77	34.969	35.453
	$^{37}_{17}\text{Cl}$	24.23	36.966	
Copper	$^{63}_{29}\text{Cu}$	69.17	62.930	63.546
	$^{65}_{29}\text{Cu}$	30.83	64.928	

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



Atomic mass indicated on entries of the Periodic Table. (public Domain; [Pubchem](#))

The **periodic table** is found on the "Resources" link in the blue bar on the left of this page or in this link:

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

Concept Review Exercises

1. Define atomic mass. Why is it considered a weighted average?
2. What is an atomic mass unit?

Answers

1. The atomic mass is an average of an element's atomic masses, weighted by the natural abundance of each isotope of that element. It is a weighted average because different isotopes have different masses.
2. An atomic mass unit is 1/12th of the mass of a ^{12}C atom.

Key Takeaway

- Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.
- The atomic mass of each element in the Periodic Table is the weighted average of the mass of all its isotopes.

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1.6: Arrangements of Electrons

Learning Objectives

- Describe how electrons are grouped within atoms.

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

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

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

Table 1.6.1: Shells and Subshells

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

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

Table 1.6.2: Number of Electrons

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

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

We use numbers to indicate which shell an electron is in. As shown in Table 1.6.1, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1s 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 **1s¹** to describe the electronic structure of hydrogen. This structure is called an **electron configuration**. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as “one-ess-one.”

Helium atoms have 2 electrons. Both electrons fit into the 1s subshell because s subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is **1s²** (spoken as “one-ess-two”).

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

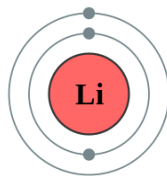


Figure 1.6.1: Shell diagram of lithium (Li) atom.

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

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

With neon, the 2p subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled s, p, and d. The d subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. However, a curious thing happens after the 3p subshell is filled: the 4s subshell begins to fill before the 3d subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms. A fourth subshell, the f subshell, is needed to complete the electron configurations for all elements. An f subshell can hold up to 14 electrons.

Electron filling always starts with 1s, the subshell closest to the nucleus. Next is 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, etc., shown in the electron shell filling order diagram in Figure 1.6.2. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

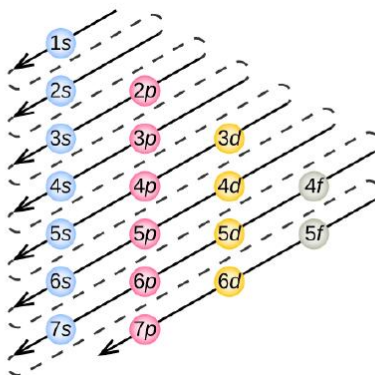


Figure 1.6.2: The order of electron filling in an atom.

✓ Example 1.6.1: Electronic Configuration of Phosphorus Atoms

Using Figure 1.6.2 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 1s subshell, 2 can go into the 2s subshell, and 6 can go into the 2p subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3s subshell, and the remaining 3 electrons can go into the 3p subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

? Exercise 1.6.1: Electronic Configuration of Chlorine Atoms

Using Figure 1.6.2 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 1s subshell, 2 can go into the 2s subshell, and 6 can go into the 2p subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3s subshell, and the remaining 5 electrons can go into the 3p subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

Since the arrangement of the periodic table is based on the electron configurations, Figure 1.6.3 provides an alternative method for determining the electron configuration. The filling order simply **begins at the top left**, with hydrogen ($Z=1$) and includes each subshell as you proceed in increasing atomic number (Z) order.

Electron Configuration Table

Group																		18
1																		2
1	H 1																	He 1s
2	Li 1 Be 2																	B 1 C 2 N 3 O 4 F 5 Ne 6
3	Na 1 Mg 2																	Al 1 Si 2 P 3 S 4 Cl 5 Ar 6
4	K 1 Ca 2	Sc 1	Ti 2	V 3	Cr 4	Mn 5	Fe 6	Co 7	Ni 8	Cu 9	Zn 10							Ga 1 Ge 2 As 3 Se 4 Br 5 Kr 6
5	Rb 1 Sr 2	Y 1	Zr 2	Nb 3	Mo 4	Tc 5	Ru 6	Rh 7	Pd 8	Ag 9	Cd 10							In 1 Sn 2 Sb 3 Te 4 I 5 Xe 6
6	Cs 1 Ba 2	La *1	Hf 2	Ta 3	W 4	Re 5	Os 6	Ir 7	Pt 8	Au 9	Hg 10							Tl 1 Pb 2 Bi 3 Po 4 At 5 Rn 6
7	Fr 1 Ra 2	Ac**1	Rf 2	Db 3	Sg 4	Bh 5	Hs 6	Mt 7	Ds 8	Rg 9	Cn 10							Nh 1 Fl 2 Mc 3 Lv 4 Ts 5 Og 6
		* Ce 1	Pr 2	Nd 3	Pm 4	Sm 5	Eu 6	Gd 7	Tb 8	Dy 9	Ho 10	Er 11	Tm 12	Yb 13	Lu 14			
		** Th 1	Pa 2	U 3	Np 4	Pu 5	Am 6	Cm 7	Bk 8	Cf 9	Es 10	Fm 11	Md 12	No 13	Lr 14			

Name → **H** 1 ← Electrons

1s ← Subshell

Figure 1.6.3: This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

For example, the first row (Period 1) contains H and He only, because only two electrons are required to fill the 1s subshell. The second row s-block, contains only two elements, Li and Be, to fill the 2s subshell. This is followed by the second row p-block, containing 6 elements (B through Ne) since six electrons are required to fill the 2p subshell. The third row is similar to the second row elements. Two electrons are needed (Na and Mg) to fill the 3s subshell and six electrons are required (Al through Ar) to complete the 3p subshell. After filling the 3p block up to Ar, we see the next subshell will be 4s (K, Ca), followed by the 3d subshell, which are filled by ten electrons (Sc through Zn). The 4p subshell is filled next by six electrons (Ga through Kr). As you

can see, the periodic table shown in Figure 1.6.3 provides a simple way to remember the order of filling the subshells in determining the electron configuration. The order of filling subshells is the same: **1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s**, etc.

✓ Example 1.6.2: Aluminum

Using Figure 1.6.3 as your guide, write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

*Start at Period 1 of the periodic table, Figure 1.6.3. Place two electrons in the 1s subshell (**1s²**).*

*Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**2s²**) and the next six electrons in the 2p subshell (**2p⁶**).*

*Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**3s²**) and the last one electron in the 3p subshell (**3p¹**).*

The electron configuration of Aluminum is **1s²2s²2p⁶3s²3p¹**

Exercise

Using Figure 1.6.3 as your guide, write the electron configuration of the atom that has 20 electrons

Answer

*Start at Period 1 of Figure 1.6.3 Place two electrons in the 1s subshell (**1s²**).*

*Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**2s²**) and the next six electrons in the 2p subshell (**2p⁶**).*

*Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**3s²**) and the next six electrons in the 3p subshell (**3p⁶**).*

*Proceed to Period 4. Place the remaining two electrons in the 4s subshell (**4s²**).*

The electron configuration is **1s²2s²2p⁶3s²3p⁶4s²**

Valence Electrons

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

In the second period elements, the two electrons in the 1s sublevel are called **inner-shell electrons** and are not involved directly in the element's reactivity or in the formation of compounds. Lithium has a single electron in the second principal energy level and so we say that lithium has one valence electron. Beryllium has two valence electrons. How many valence electrons does boron have? You must recognize that the second principal energy level consists of both the 2s and the 2p sublevels and so the answer is three. In fact, the number of valence electrons goes up by one for each step across a period until the last element is reached. Neon, with its configuration ending in 2s²2p⁶, has eight valence electrons.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a 1s²2s²2p⁶3s¹ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** (Figure \PageIndex4). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, (1s²2s²2p⁶) and our abbreviated or condensed configuration is [Ne]3s¹.

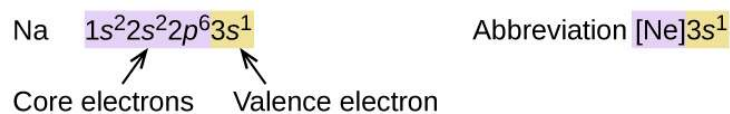
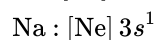


Figure 1.6.4: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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



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

✓ Example 1.6.3

Examine the electron configuration of neutral phosphorus atoms in Example 1.6.1, $1s^2 2s^2 2p^6 3s^2 3p^3$ and write the abbreviated notation.

Solution

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

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

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by $[\text{Ne}]$ (see Figure 1.6.3). Abbreviated notation is : $[\text{Ne}] 3s^2 3p^3$

? Exercise 1.6.3

Examine the electron configuration of neutral calcium atom (Exercise 1.6.2), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

Answer

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

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by $[\text{Ar}]$, see Figure 1.6.3 The abbreviated notation is: $[\text{Ar}] 4s^2$

✓ Example 1.6.4

Based on their respective locations in the periodic table (use Figure 1.6.3), determine the number of valence electrons and the valence shell configuration of elements A, B and C.

Solution

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

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

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

Exercise

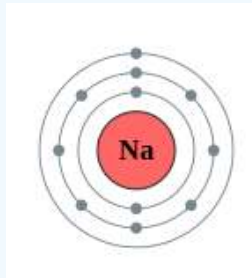
Using the location of Na in the periodic table (Figure 1.6.3), draw the shell diagram of sodium atom.

Answer

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

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

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



Concept Review Exercises

1. How are electrons organized in atoms?
2. What information does an electron configuration convey?
3. What is the difference between core electrons and valence electrons?

Answers

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

Key Takeaway

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

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1.7: The Periodic Table

Learning Objectives

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

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

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

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

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure 1.7.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

Period	Group																18																			
1	1												2		18																					
1	1												2		18																					
2	3		4												13		14	15	16	17	18															
2	3		4												13		14	15	16	17	18															
3	11		12												13		14	15	16	17	18															
3	11		12												13		14	15	16	17	18															
4	19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36	
4	19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36	
5	37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54	
5	37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54	
6	55		56		*		72		73		74		75		76		77		78		79		80		81		82		83		84		85		86	
6	55		56		*		72		73		74		75		76		77		78		79		80		81		82		83		84		85		86	
7	87		88		**		104		105		106		107		108		109		110		111		112		113		114		115		116		117		118	
7	87		88		**		104		105		106		107		108		109		110		111		112		113		114		115		116		117		118	
	*		57		58		59		60		61		62		63		64		65		66		67		68		69		70		71					
	*		57		58		59		60		61		62		63		64		65		66		67		68		69		70		71					
	**		89		90		91		92		93		94		95		96		97		98		99		100		101		102		103					
	**		89		90		91		92		93		94		95		96		97		98		99		100		101		102		103					

Figure 1.7.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

Features of the Periodic Table

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

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

Metals, Nonmetals and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 1.7.2. 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 1.7.2, **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.

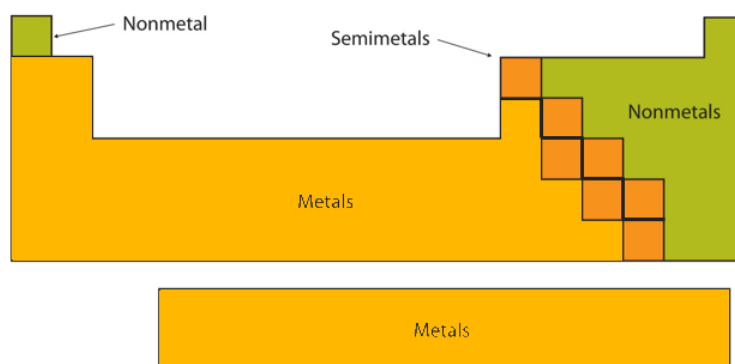


Figure 1.7.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

✓ Example 1.7.1

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

Solution

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

Exercise

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

Answer

metal

Representative, Transition and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 1.7.3. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns

contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

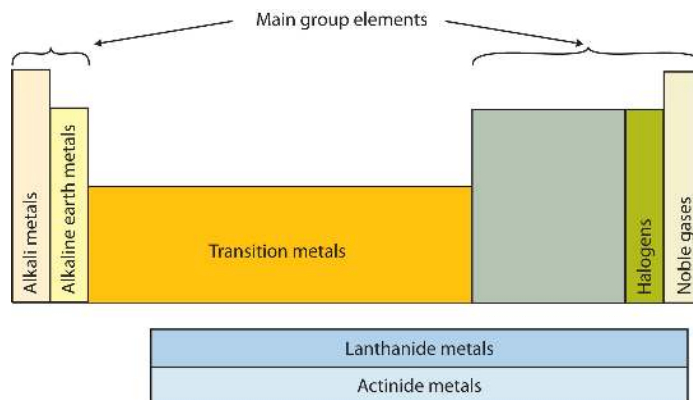


Figure 1.7.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

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

To Your Health: Transition Metals in the Body

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

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

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

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

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

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

Group 1: The Alkali Metals

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

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

To Your Health: Radon

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

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

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

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure 1.7.4. Starting with the first period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry**.

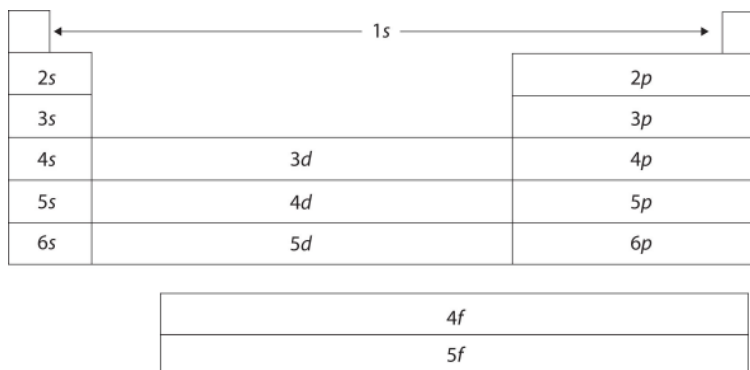


Figure 1.7.4 The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

✓ Example 1.7.1

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

- the alkaline earth metals
- the column of elements headed by carbon

Answer a

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

Answer b

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

? Exercise 1.7.1

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

- the halogens
- the column of elements headed by oxygen

Answer a

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

Answer b

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

Valence Electrons and Group Number

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

Table 1.7.1. The Group number and the number of valence electrons.

Periodic table group	Valence electrons
Group 1 (I) (alkali metals)	1

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

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

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

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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1.8: The Classification of Matter

Learning Objectives

- Use physical and chemical properties, including phase, to describe matter.
- Identify a sample of matter as an element, a compound, or a mixture.

Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.

Physical and Chemical Properties

The properties that chemists use to describe matter fall into two general categories. **Physical properties** are characteristics that describe matter. They include characteristics such as size, shape, color, and mass. These characteristics can be observed or measured without changing the *identity* of the matter in question. **Chemical properties** are characteristics that describe how matter changes its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties.



Figure 1.8.1: (left) Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

Elements and Compounds

Any sample of matter that has the *same physical and chemical properties throughout* the sample is called a **substance**. There are two types of substances. A substance that cannot be broken down into chemically simpler components is called an **element**. Aluminum, which is used in soda cans and is represented by the symbol Al, is an element. A substance that can be broken down into chemically simpler components (because it consists of more than one element) is called a **compound**. Water is a compound composed of the elements hydrogen and oxygen and is described by the chemical formula, H_2O . Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

Sometimes the word *pure* is used to describe a substance, but this is not absolutely necessary. By definition, any single substance, element or compound is *pure*.

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

However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the *microscopic or particle viewpoint*. We will see examples of both macroscopic and particle viewpoints throughout this book (Figure 1.8.2).

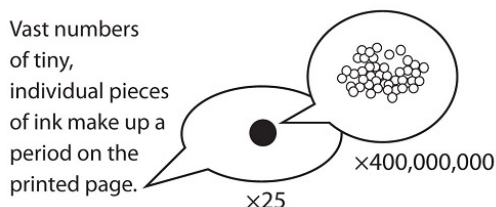


Figure 1.8.2: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The $\times 25$ and $\times 400,000,000$ indicate the number of times the image is magnified.

Mixtures

A material composed of two or more substances is a **mixture**. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called **heterogeneous mixtures**. In some mixtures, the components are so intimately combined that they act like a single substance (even though they are not). Mixtures with a consistent or uniform composition throughout are called **homogeneous mixtures** (or solutions). For example, when sugar is dissolved in water to form a liquid solution, the individual properties of the components cannot be distinguished. Other examples of homogeneous mixtures include solid solutions, like the metal alloy steel, and gaseous solutions, like air which is a mixture of mainly nitrogen and oxygen.

✓ Example 1.8.1

How would a chemist categorize each example of matter?

- saltwater
- soil
- water
- oxygen

Answer a

Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a *homogeneous mixture*, or a solution.

Answer b

Soil is composed of small pieces of a variety of materials, so it is a *heterogeneous mixture*.

Answer c

Water is a *substance*; more specifically, because water is composed of hydrogen and oxygen, it is a *compound*.

Answer d

Oxygen, a *substance*, is an *element*.

? Exercise 1.8.2

How would a chemist categorize each example of matter?

- breakfast coffee
- hydrogen
- an egg

Answer a

homogeneous mixture or solution

Answer b

element

Answer c

heterogeneous mixture

Phases or Physical States of Matter

All matter can be further classified by one of three physical **states** or **phases**, solid, liquid or gas. These three descriptions each imply that the matter has certain physical properties when in these states. A solid has a definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers.

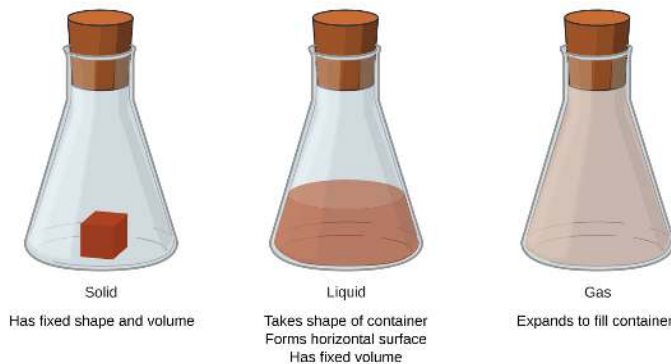


Figure 1.8.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

A beaker labeled solid contains a cube of red matter and says has fixed shape and volume. A beaker labeled liquid contains a brownish-red colored liquid. This beaker says takes shape of container, forms horizontal surfaces, has fixed volume. The beaker labeled gas is filled with a light brown gas. This beaker says expands to fill container.

We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas) (Figure 1.8.2).



Figure 1.8.5: Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. (CC BY-SA 3.0 Unported; Markus Schweiss via Wikipedia)

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a **phase change**, a physical process in which a substance changes from one phase to another (Figure 1.8.5). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 1.8.1.

Table 1.8.1: Phase Changes

Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation

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

Figure 1.8.3 illustrates the relationships between the different ways matter can be classified.

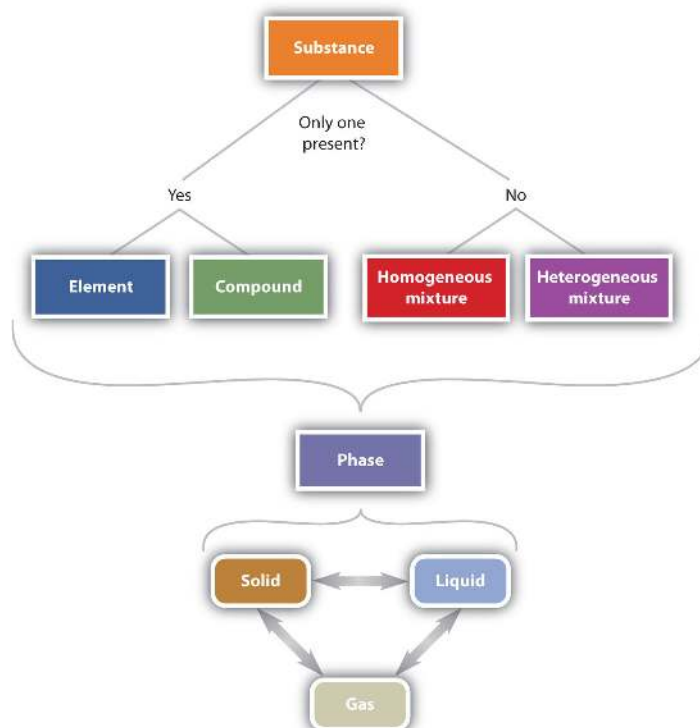


Figure 1.8.6: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture or a heterogeneous mixture. From these choices, the substance can be in a certain phase. It can either be solid, liquid, or gas, and each phase can go from one to another.

Concept Review Exercises

1. Explain the differences between the physical properties of matter and the chemical properties of matter.
2. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
3. Give at least two examples of a phase change and state the phases involved in each.

Answers

1. Physical properties describe the existence of matter, and chemical properties describe how substances change into other substances.
2. A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.
3. solid to liquid (melting) and liquid to gas (boiling) (answers will vary)

Key Takeaways

- Matter can be described with both physical properties and chemical properties.
- Matter can be identified as an element, a compound, or a mixture

? Exercise 1.8.3

Does each statement refer to a chemical property or a physical property?

1. Balsa is a very light wood.
2. If held in a flame, magnesium metal burns in air.
3. Mercury has a density of 13.6 g/mL.
4. Human blood is red.

Answer

1. physical property
2. chemical property
3. physical property
4. physical property

? Exercise 1.8.4

Does each statement refer to a chemical property or a physical property?

1. The elements sodium and chlorine can combine to make table salt.
2. The metal tungsten does not melt until its temperature exceeds 3,000°C.
3. The ingestion of ethyl alcohol can lead to disorientation and confusion.
4. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water

Answer

1. chemical property
2. physical property
3. chemical property
4. physical property

? Exercise 1.8.5

Define *element*. How does it differ from a compound?

Answer

An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

? Exercise 1.8.6

Define *compound*. How does it differ from an element?

Answer

A compound is composed of two or more elements combined in a fixed ratio. An element is the simplest chemical substance.

? Exercise 1.8.7

Give two examples of a heterogeneous mixture.

Answer

example response: a salt and pepper mix and a bowl of cereal

? Exercise 1.8.8

Give two examples of a homogeneous mixture.

Answer

example response: vinegar and rubbing alcohol

? Exercise 1.8.9

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

1. xenon, a substance that cannot be broken down into chemically simpler components
2. blood, a substance composed of several types of cells suspended in a salty solution called plasma
3. water, a substance composed of hydrogen and oxygen

Answer

1. element
2. heterogeneous mixture
3. compound

? Exercise 1.8.10

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

1. sugar, a substance composed of carbon, hydrogen, and oxygen
2. hydrogen, the simplest chemical substance
3. dirt, a combination of rocks and decaying plant matter

Answer

1. compound
2. element
3. heterogeneous mixture

? Exercise 1.8.11

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

1. air, primarily a mixture of nitrogen and oxygen
2. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
3. tartaric acid, a substance composed of carbon, hydrogen, and oxygen

Answer

1. heterogeneous mixture
2. solution
3. compound

? Exercise 1.8.12

What word describes each phase change?

1. solid to liquid
2. liquid to gas
3. solid to gas

Answer

1. melting or fusion
2. boiling or evaporation
3. sublimation

? Exercise 1.8.13

1. What word describes each phase change?
 1. liquid to solid
 2. gas to liquid
 3. gas to solid

Answer

1. freezing
2. condensation
3. deposition

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CHAPTER OVERVIEW

2: Compounds - Ionic and Molecular

2.1: Two Types of Bonding

2.2: Ions

2.2.1: Formulas for Ionic Compounds

2.2.2: Ionic Nomenclature

2.2.3: Characteristics of Ionic Compounds

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2.1: Two Types of Bonding

Learning Objectives

- Define the octet rule.
- Describe how ionic bonds are formed.

Atoms can join together by forming a chemical bond, which is a very strong attraction between two atoms. Chemical bonds are formed when electrons in different atoms interact with each other to make an arrangement that is more stable than when the atoms are apart.

What causes atoms to make a chemical bond with other atoms, rather than remaining as individual atoms? A clue comes by considering the noble gas elements, the rightmost column of the periodic table. These elements—helium, neon, argon, krypton, xenon, and radon—do not form compounds very easily, which suggests that they are especially stable as lone atoms. What else do the noble gas elements have in common? Except for helium, they all have eight valence electrons. Chemists have concluded that atoms are especially stable if they have eight electrons in their outermost shell. This useful rule of thumb is called the **octet rule**, and it is a key to understanding why compounds form.

Of the noble gases, only krypton, xenon, and radon have been found to make compounds.

There are two ways for an atom that does not have an octet of valence electrons to obtain an octet in its outer shell. One way is the transfer of electrons between two atoms until all atoms have octets. Because some atoms will lose electrons and some atoms will gain electrons, there is no overall change in the number of electrons, but individual atoms acquire a nonzero electric charge. Those that lose electrons become positively charged, and those that gain electrons become negatively charged. Charged atoms are called ions. Because opposite charges attract (while like charges repel), these oppositely charged ions attract each other, forming **ionic bonds**. The resulting compounds are called **ionic compounds** and are the primary subject of this chapter.

The second way for an atom to obtain an octet of electrons is by sharing electrons with another atom. These shared electrons simultaneously occupy the outermost shell of more than one atom. The bond made by electron sharing is called a **covalent bond**.

Despite our focus on the octet rule, we must remember that for small atoms, such as hydrogen, helium, and lithium, the first shell is, or becomes, the outermost shell and hold only two electrons. Therefore, these atoms satisfy a “**duet rule**” rather than the octet rule.

✓ Example 2.1.1

A sodium atom has one valence electron. Do you think it is more likely for a sodium atom to lose one electron or gain seven electrons to obtain an octet?

Solution

Although either event is possible, a sodium atom is more likely to lose its single valence electron. When that happens, it becomes an ion with a net positive charge. This can be illustrated as follows:

Table explaining the solution to the example.

Sodium atom		Sodium ion	
11 protons	11+	11 protons	11+
11 electrons	11−	10 electrons	10−
	0 overall charge		+1 overall charge

? Exercise 2.1.1

A fluorine atom has seven valence electrons. Do you think it is more likely for a fluorine atom to lose seven electrons or gain one electron to obtain an octet? Write the formula of the resulting ion.

Answer

The process that involves less number of electrons is more favorable. Fluorine would gain one electron. The formula of the resulting ion is F^- .

Key Takeaways

- Atoms have a tendency to have eight electrons in their valence shell.
- The attraction of oppositely charged ions is what makes ionic bonds.

Exercises

1. What is the octet rule?
2. How are ionic bonds formed?
3. Why is an ionic compound unlikely to consist of two positively charged ions?
4. Why is an ionic compound unlikely to consist of two negatively charged ions?
5. A calcium atom has two valence electrons. Do you think it will lose two electrons or gain six electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.
6. An aluminum atom has three valence electrons. Do you think it will lose three electrons or gain five electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.
7. A selenium atom has six valence electrons. Do you think it will lose six electrons or gain two electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.
8. An iodine atom has seven valence electrons. Do you think it will lose seven electrons or gain one electron to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

Answers

1. The octet rule is the concept that atoms tend to have eight electrons in their valence electron shell.
2. Ionic bonds are formed by the attraction between oppositely charged ions.
3. Positive charges repel each other, so an ionic compound is not likely between two positively charged ions.
4. Negative charges repel each other also.
5. Ca atom is more likely to lose two electrons. It will become Ca^{2+} ion.
6. An Al atom is more likely to lose three electrons. It will become Al^{3+} ion.
7. Selenium is more likely to gain two electrons. It will become Se^{2-} ion.
8. Iodine is more likely to gain one electron. It will become I^- ion.

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2.2: Ions

Learning Objectives

- Define the two types of ions.
- Use Lewis diagrams to illustrate ion formation.

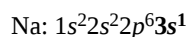
Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called cations. Most metals become cations when they make ionic compounds.

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called anions. Most nonmetals become anions when they make ionic compounds.

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

Electron Transfer

We can use electron configurations to illustrate the electron transfer process between sodium atoms and chlorine atoms.



As demonstrated here, a sodium atom (Na) has one valence electron in the third principal energy level. It is likely to achieve an octet in its outermost shell by losing its one valence electron. The cation produced in this way, Na^+ , is called the sodium ion to distinguish it from the element. The sodium ion, Na^+ , has the electron configuration with an octet of electrons from the second principal energy level. It is now the same as that of the noble gas neon. The term **isoelectronic** refers to an atom and an ion of a different atom (or two different ions) that have the same electron configuration. The sodium ion is isoelectronic with the neon atom. The equation below illustrates this process.

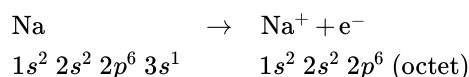


Figure 2.2.1 is a graphical depiction of this process.

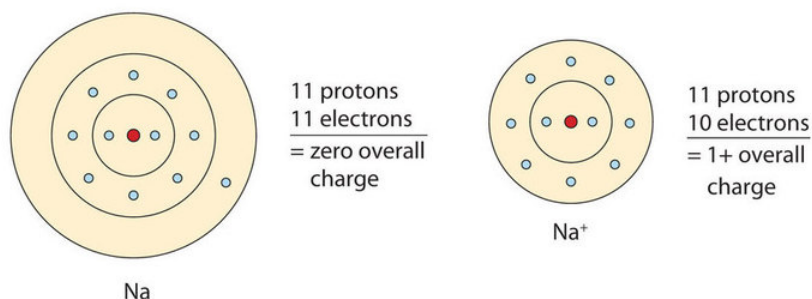


Figure 2.2.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Now, let's consider chlorine atom, $\text{Cl: } 1s^2 2s^2 2p^6 3s^2 3p^5$

Only one more electron is needed to achieve an octet in chlorine's valence shell. When a chlorine atom gains an electron, its outermost principal energy level achieves an octet. In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^- , is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. This process is illustrated below. (In table salt, this electron comes from the sodium atom.)

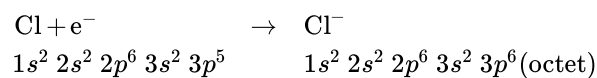


Figure 2.2.2 is a graphical depiction of this process.

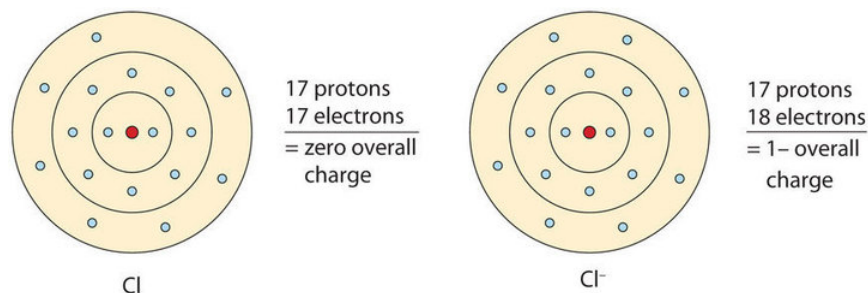


Figure 2.2.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1- charge.

With two oppositely charged ions, there is an electrostatic attraction between them because opposite charges attract. The resulting combination is the compound sodium chloride. Notice that there are no leftover electrons. The number of electrons lost by the sodium atom (one) equals the number of electrons gained by the chlorine atom (one), so the compound is electrically neutral. In macroscopic samples of sodium chloride, there are billions and billions of sodium and chloride ions, although there is always the same number of cations and anions.

✓ Example 2.2.1

Write the electron configuration of aluminum atom (atomic number 13). How many electrons must Al lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

Solution

The electron configuration of Al atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. The second shell has octet ($2s^2 2p^6$) while the valence shell has 3 electrons ($3s^2 3p^1$). Al can achieve octet by losing the 3 valence electrons. The resulting cation is Al^{3+} with electron configuration, $1s^2 2s^2 2p^6$.

Exercise

Write the electron configuration of oxygen atom (atomic number 8). How many electrons must O lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

Answer

The electron configuration of O atom is $1s^2 2s^2 2p^4$. The second shell has six electrons ($2s^2 2p^4$) and needs two electrons to achieve octet. Oxygen will gain 2 electrons. The resulting anion is O^{2-} with electron configuration, $1s^2 2s^2 2p^6$.

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1- charge. Figure 2.2.3 shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion.

1A						8A
H ⁺						
	2A	3A	4A	5A	6A	7A
Li ⁺				N ³⁻	O ²⁻	F ⁻
Na ⁺	Mg ²⁺	Al ³⁺		P ³⁻	S ²⁻	Cl ⁻
K ⁺	Ca ²⁺				Se ²⁻	Br ⁻
Rb ⁺	Sr ²⁺					I ⁻

Figure 2.2.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

✓ Example 2.2.2

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

- Mg⁺
- K⁺

Solution

(a) Mg is in Group 2A and has two valence electrons. It achieves octet by losing two electrons to form Mg²⁺ cation. Losing only one electron to form Mg⁺ does not make an octet, hence, Mg⁺ is not likely to form.

Exercise

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

- S³⁻
- N³⁻

Answer

(a) S is in Group 6A and has six valence electrons. It achieves octet by gaining two electrons to form S²⁻ anion. Gaining three electrons to form S³⁻ does not make it octet, hence, S³⁻ is not likely to form.

Lewis Diagrams

Chemists use simple diagrams to show an atom's valence electrons and how they transfer. These diagrams have two advantages over the electron shell diagrams. First, they show only valence electrons. Second, instead of having a circle around the chemical symbol to represent the electron shell, they have up to eight dots around the symbol; each dot represents a valence electron. These dots are arranged to the right and left and above and below the symbol, **with no more than two dots on a side**. For example, the representation for sodium is as follows:



and the representation for chlorine is as follows:



For the above diagrams, it does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. To write an element's Lewis dot symbol, place the dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. In other words, **place the dots singly on each side before pairing them**. The Lewis electron dot diagram of fluorine, for example, with seven valence electrons, is constructed as follows:

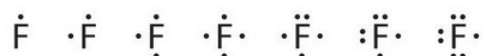
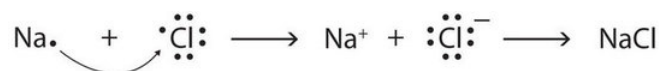


Figure 2.2.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



Figure 2.2.4: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

The transfer of electrons can be illustrated easily with Lewis diagrams:



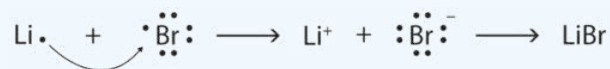
In representing the final formula, the dots are omitted.

✓ Example 2.2.3

Starting with lithium and bromine atoms, use Lewis diagrams to show the formation of the ionic compound LiBr.

Solution

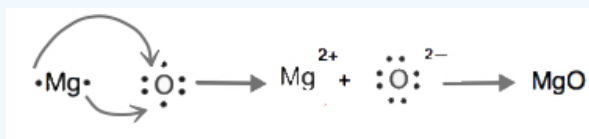
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it will have the same Lewis diagram that chlorine has. Therefore,



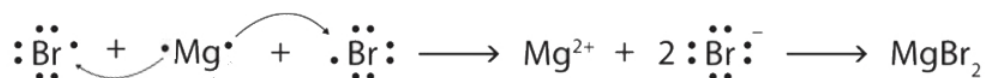
? Exercise 2.2.3

Starting with magnesium and oxygen atoms, use Lewis diagrams to show the formation of the ionic compound MgO.

Answer



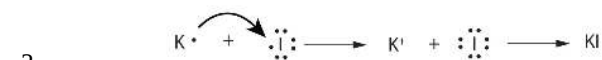
Some ionic compounds have different numbers of cations and anions. In those cases, electron transfer occurs between more than one atom. For example, here is the formation of MgBr_2 :



7. Draw Lewis diagrams for the ions listed in Exercise 6. Also include Lewis diagrams for the respective neutral atoms as a comparison.
8. Using Lewis diagrams, show the electron transfer for the formation of LiF.
9. Using Lewis diagrams, show the electron transfer for the formation of MgO.
10. Using Lewis diagrams, show the electron transfer for the formation of Li_2O .
11. What characteristic charge do atoms in the first column of the periodic table have when they become ions?
12. What characteristic charge do atoms in the second column of the periodic table have when they become ions?
13. What characteristic charge do atoms in the third-to-last column of the periodic table have when they become ions?
14. What characteristic charge do atoms in the next-to-last column of the periodic table have when they become ions?

Answers

1. Cations (positive charged) and anions (negative charged).



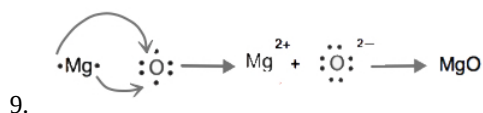
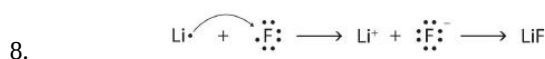
3.
 - a. 1+
 - b. 2-
 - c. 2+
 - d. 1-

4.
 - a. cation
 - b. anion
 - c. neither
 - d. cation

5.
 - a. neither
 - b. anion
 - c. anion
 - d. cation

6.
 - a. $1s^2$
 - b. $1s^2 2s^2 2p^6$
 - c. $1s^2 2s^2 2p^6$
 - d. $1s^2 2s^2 2p^6 3s^2 3p^6$

7.
 - a. $\text{Li}^\bullet, \text{Li}^+$
 - b. $\cdot\text{Mg}\cdot, \text{Mg}^{2+}$
 - c. $:\ddot{\text{F}}\cdot, :\ddot{\text{F}}:^-$
 - d. $:\ddot{\text{S}}\cdot, :\ddot{\text{S}}:^{2-}$



10.
$$\text{Li}\cdot + \cdot\ddot{\text{O}}\cdot + \cdot\text{Li} \longrightarrow 2\text{Li}^+ + :\ddot{\text{O}}:^{2-} \longrightarrow \text{Li}_2\text{O}$$
11. 1+
12. 2+
13. 2-
14. 1-

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2.2.1: Formulas for Ionic Compounds

Learning Objectives

- Write the chemical formula for a simple ionic compound.
- Recognize polyatomic ions in chemical formulas.

We have already encountered some chemical formulas for simple ionic compounds. A chemical formula is a concise list of the elements in a compound and the ratios of these elements. To better understand what a chemical formula means, we must consider how an ionic compound is constructed from its ions.

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 2.2.1.1). 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, 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 2.2.1.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

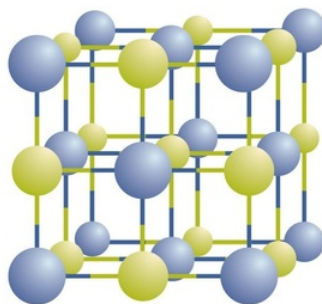


Figure 2.2.1.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

The formula for an ionic compound follows several conventions:

- 1) The **cation** is written **before** the **anion**. For example, we write **NaCl**, not **ClNa**. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal.
- 2) **Charges are not written** in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always has **a net zero charge**, meaning the total positive charge must equal the total negative charge. To determine the proper formula of any combination of ions, determine how many of each ion is needed to balance the total positive and negative charges in the compound.

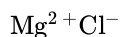
This rule is ultimately based on the fact that matter is, overall, electrically neutral.

By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

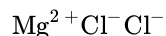
If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the bromide ion has a 1− charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is LiBr.

When an ionic compound is formed from magnesium and oxygen, the magnesium ion has a 2+ charge, and the oxygen atom has a 2− charge. Although both of these ions have higher charges than the ions in lithium bromide, they still balance each other in a one-to-one ratio. Therefore, the proper formula for this ionic compound is MgO.

Now consider the ionic compound formed by magnesium and chlorine. A magnesium ion has a 2+ charge, while a chlorine ion has a 1− charge:



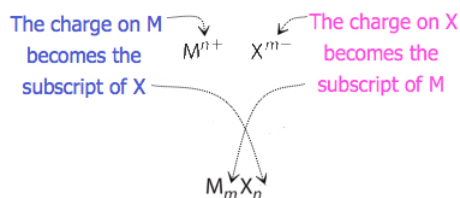
Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:



Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as MgClCl , but the convention is to use a numerical subscript when there is more than one ion of a given type— MgCl_2 . This chemical formula says that there are one magnesium ion and two chloride ions in this formula. (Do not read the “ Cl_2 ” part of the formula as a molecule of the diatomic elemental chlorine. Chlorine does not exist as a diatomic element in this compound. Rather, it exists as two individual chloride ions.) By convention, the **lowest whole number ratio** is used in the formulas of ionic compounds. The formula Mg_2Cl_4 has balanced charges with the ions in a 1:2 ratio, but it is not the lowest whole number ratio.

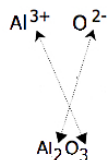
By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as Hg_2^{2+} .

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.



The image shows M with a charge of $n+$ and X with a charge of $m-$. The charge on the M becomes the subscript of X, and the charge on X becomes the subscript of M, making the final product M subscript m X subscript n.

Write the formula for the compound formed by aluminum and oxygen.



The image asks to write the formula for the compound formed by aluminum and oxygen. It shows Al with a charge of $3+$ and O with a charge of $2-$. By crossing charges, the final result is Al subscript 2 O subscript 3.

Figure 2.2.1.2: 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 **PbO_2** . The empirical formula has one Pb^{4+} ion and two O^{2-} ions.

✓ Example 2.2.1.1

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

- the sodium ion and the sulfur ion
- the aluminum ion and the fluoride ion
- the $3+$ iron ion and the oxygen ion

Solution

- To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfur ion. Rather than writing the formula as NaNaS , we shorten it by convention to Na_2S .
- The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluorine 1− ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as AlF_3 .
- Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2− charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2− oxygen ions will give 6−, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is Fe_2O_3 . Alternatively, use the crossing charges method shown in Figure 3.3.2.

? Exercise 2.2.1.1

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

- the calcium ion and the oxygen ion
- the 2+ copper ion and the sulfur ion
- the 1+ copper ion and the sulfur ion

Answer a:



Answer b:



Answer c:

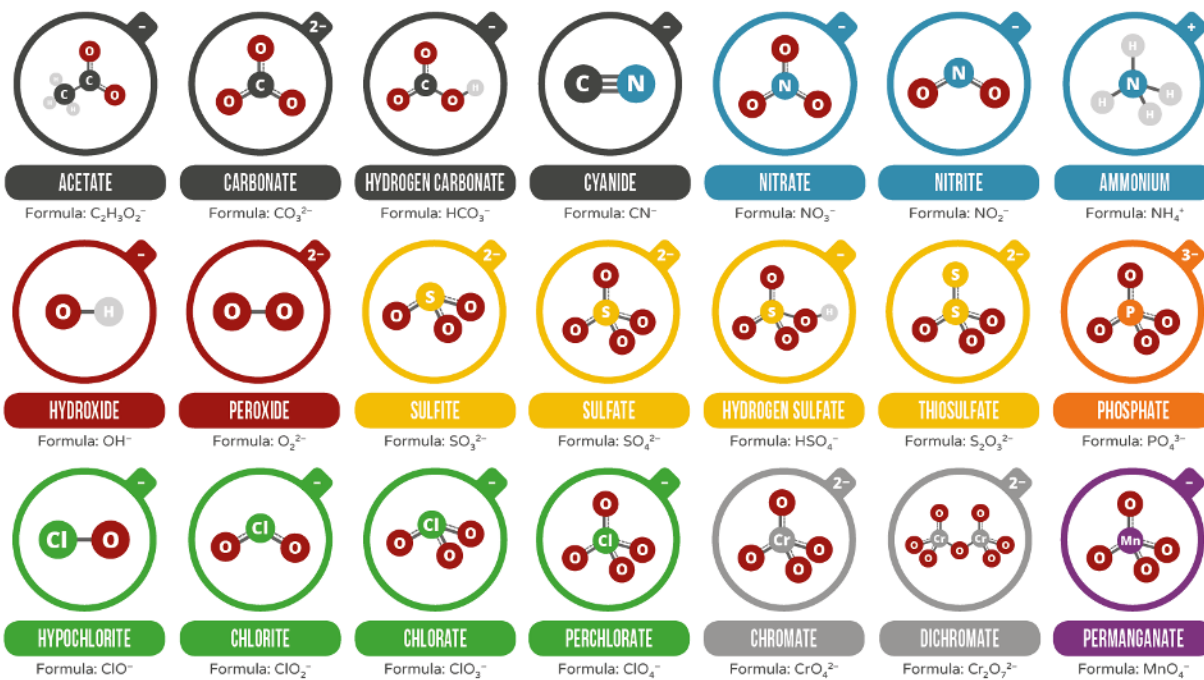


Polyatomic Ions

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 Lewis structures, names and formulas of some polyatomic ions are found in Table 3.3.1.

POLYATOMIC IONS: NAMES, FORMULAE & CHARGES

A polyatomic ion is a charged species consisting of two or more atoms covalently bonded together. Here's a guide to some of the most common examples!



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Table 2.2.1.1: Some Polyatomic Ions

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 2.2.1.2 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. Figure 2.2.1.2 lists the most common polyatomic ions.

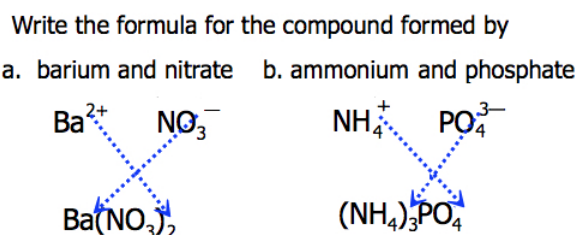
Table 2.2.1.2: Ion Names and Ion Formulas of Common Polyatomic Ions

Ion Name	Ion Formula
ammonium ion	NH_4^{+1}
hydroxide ion	OH^{-1}
cyanide ion	CN^{-1}
carbonate ion	CO_3^{-2}
bicarbonate or hydrogen carbonate	HCO_3^-
acetate ion	$\text{C}_2\text{H}_3\text{O}_2^{-1}$ or $\text{CH}_3\text{CO}_2^{-1}$
nitrate ion	NO_3^{-1}
nitrite ion	NO_2^{-1}
sulfate ion	SO_4^{-2}
sulfite ion	SO_3^{-2}
phosphate ion	PO_4^{-3}

Ion Name	Ion Formula
phosphite ion	PO_3^{-3}

Note that only one polyatomic ion in this Table, the ammonium ion (NH_4^{+1}), is a cation. This polyatomic ion contains one nitrogen and four hydrogens that collectively bear a +1 charge. 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 particles. 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. As has been repeatedly emphasized in several sections of this text, no two chemical formulas should share a common chemical name. Hence, a new set of suffixes are used, including "-ate" and "-ite". You are not expected to memorize the names of the polyatomic ions, but should be able to use them in naming compounds.

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. Two examples are shown below:



The image asks a two-part question: Write the formula for the compound formed by (a) barium and nitrate, and (b) ammonium and phosphate. For (a), Ba has a charge of 2+ and NO_3 has a charge of -1. By crossing charges, the formula is $\text{Ba}(\text{NO}_3)_2$. For (b), NH_4 has a charge of +1 and PO_4 has a charge of 3-, so by crossing charges the formula is $(\text{NH}_4)_3\text{PO}_4$.

✓ Example 2.2.1.2

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

- the potassium ion and the sulfate ion
- the calcium ion and the nitrate ion

Solution

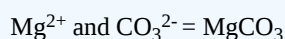
- Potassium ions have a charge of 1+, while sulfate ions have a charge of 2-. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4 .
- Calcium ions have a charge of 2+, while nitrate ions have a charge of 1-. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $\text{Ca}(\text{NO}_3)_2$ as the formula for this ionic compound.

? Exercise 2.2.1.2

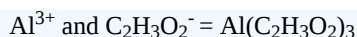
Write the chemical formula for an ionic compound composed of each pair of ions.

- the magnesium ion and the carbonate ion
- the aluminum ion and the acetate ion

Answer a:



Answer b:



Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between **metal and nonmetal** elements are usually **ionic**. For example, CaBr_2 contains a metallic element (calcium, a group 2A metal) and a nonmetallic element (bromine, a group 7A nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 5A, and oxygen, from group 6A). It is not an ionic compound; it belongs to the category of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a **polyatomic ion** in a compound, the compound is **ionic**. For example, if you see the formula $\text{Ba}(\text{NO}_3)_2$, you may recognize the “ NO_3 ” part as the nitrate ion, NO_3^- . (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the Ba^{2+} ion, with the 2+ charge balancing the overall 2- charge from the two nitrate ions. Thus, this compound is also ionic.

✓ Example 2.2.1.3

Identify each compound as ionic or not ionic.

- Na_2O
- PCl_3
- NH_4Cl
- OF_2

Solution

- Sodium is a metal, and oxygen is a nonmetal; therefore, Na_2O is expected to be ionic.
- Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.
- The NH_4 in the formula represents the ammonium ion, NH_4^+ , which indicates that this compound is ionic.
- Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.

? Exercise 2.2.1.3

Identify each compound as ionic or not ionic.

- N_2O
- FeCl_3
- $(\text{NH}_4)_3\text{PO}_4$
- SOCl_2

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Looking Closer: Blood and Seawater

Saltwater solutions are important to us. Many cooking applications involve boiling in salted water. A common saying for the salted water is that we "bring the sea to the kitchen." In addition, there is recognition that blood and seawater have similar compositions. All of these liquids have ionic compounds dissolved in them. The similarity may be more than mere coincidence; many scientists think that the first forms of life on Earth arose in the oceans. A closer look, however, shows that blood and seawater are quite different. A 0.9% solution of sodium chloride approximates the salt concentration found in blood. In contrast, seawater is principally a 3% sodium chloride solution, over three times the concentration in blood. Here is a comparison of the amounts of ions in blood and seawater:

Table showing a comparison of the amounts of ions in blood and seawater.

Ion	Percent in Seawater	Percent in Blood
Na^+	2.36	0.322
Cl^-	1.94	0.366
Mg^{2+}	0.13	0.002
SO_4^{2-}	0.09	—
K^+	0.04	0.016
Ca^{2+}	0.04	0.0096
HCO_3^-	0.002	0.165
$\text{HPO}_4^{2-}, \text{H}_2\text{PO}_4^-$	—	0.01

Most ions are more abundant in seawater than they are in blood, with some important exceptions. There are far more hydrogen carbonate ions (HCO_3^-) in blood than in seawater. This difference is significant because the hydrogen carbonate ion and some related ions have a crucial role in controlling the acid-base properties of blood. The amount of hydrogen phosphate ions— HPO_4^{2-} and H_2PO_4^- —in seawater is very low, but they are present in higher amounts in blood, where they also affect acid-base properties. Another notable difference is that blood does not have significant amounts of the sulfate ion (SO_4^{2-}), but this ion is present in seawater.

Key Takeaways

- Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge.
- Groups of atoms with an overall charge, called polyatomic ions, also exist.

EXERCISES

1. What information is contained in the formula of an ionic compound?
 - Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?

Group 1: Complete enough of these to feel comfortable with the formation of ionic compounds from their ions. Tip: use the crisscross method as described above.

3. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Mg^{2+} and I^-
- b. Na^+ and O^{2-}

4. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Na^+ and Br^-
- b. Mg^{2+} and Br^-
- c. Mg^{2+} and S^{2-}

5. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. K^+ and Cl^-
- b. Mg^{2+} and Cl^-
- c. Mg^{2+} and Se^{2-}

6. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Na^+ and N^{3-}
- b. Mg^{2+} and N^{3-}
- c. Al^{3+} and S^{2-}

7. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Li^+ and N^{3-}
- b. Mg^{2+} and P^{3-}
- c. Li^+ and P^{3-}

8. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Fe^{3+} and Br^-
- b. Fe^{2+} and Br^-
- c. Au^{3+} and S^{2-}
- d. Au^+ and S^{2-}

9. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Cr^{3+} and O^{2-}
- b. Cr^{2+} and O^{2-}
- c. Pb^{2+} and Cl^-
- d. Pb^{4+} and Cl^-

10. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. Cr^{3+} and NO_3^-
- b. Fe^{2+} and PO_4^{3-}
- c. Ca^{2+} and CrO_4^{2-}
- d. Al^{3+} and OH^-

11. Write the chemical formula for the ionic compound formed by each pair of ions.

- a. NH_4^+ and NO_3^-
- b. H^+ and $\text{Cr}_2\text{O}_7^{2-}$
- c. Cu^+ and CO_3^{2-}
- d. Na^+ and HCO_3^-

Group 2: Complete both of these questions.

12. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

- a. Ba and S
- b. Cs and I

13. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

- a. K and S
- b. Sc and Br

Group 3: Complete enough of these to feel comfortable with recognizing ionic compounds on sight.

14. Which compounds would you predict to be ionic?

- a. Li_2O
- b. $(\text{NH}_4)_2\text{O}$

- c. CO_2
- d. FeSO_3
- e. C_6H_6
- f. $\text{C}_2\text{H}_6\text{O}$

15. Which compounds would you predict to be ionic?

- a. $\text{Ba}(\text{OH})_2$
- b. CH_2O
- c. NH_2CONH_2
- d. $(\text{NH}_4)_2\text{CrO}_4$
- e. C_8H_{18}
- f. NH_3

Answers

1. the ratio of each kind of ion in the compound

2. Sometimes more than one ion is needed to balance the charge on the other ion in an ionic compound.

3.

- a. MgI_2
- b. Na_2O

4.

- a. NaBr
- b. MgBr_2
- c. MgS

5.

- a. KCl
- b. MgCl_2
- c. MgSe

6.

- a. Na_3N
- b. Mg_3N_2
- c. Al_2S_3

7.

- a. Li_3N
- b. Mg_3P_2
- c. Li_3P

8.

- a. FeBr_3
- b. FeBr_2
- c. Au_2S_3
- d. Au_2S

9.

- a. Cr_2O_3
- b. CrO
- c. PbCl_2
- d. PbCl_4

10.

- a. $\text{Cr}(\text{NO}_3)_3$
- b. $\text{Fe}_3(\text{PO}_4)_2$
- c. CaCrO_4
- d. $\text{Al}(\text{OH})_3$

11.

- a. NH_4NO_3
- b. $\text{H}_2\text{Cr}_2\text{O}_7$
- c. Cu_2CO_3
- d. NaHCO_3

12.

- a. Ba^{2+} , S^{2-} , BaS
- b. Cs^+ , I^- , CsI

13.

- a. K^+ , S^{2-} , K_2S
- b. Sc^{3+} , Br^- , ScBr_3

14.

- a. ionic
- b. ionic
- c. not ionic
- d. ionic
- e. not ionic
- f. not ionic

15.

- a. ionic
- b. not ionic
- c. not ionic
- d. ionic
- e. not ionic
- f. not ionic

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2.2.2: Ionic Nomenclature

Learning Objectives

- To use the rules for naming ionic compounds

After learning a few more details about the names of individual ions, you will be 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 Ions

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

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

There are two ways to make this distinction. In the simpler, more modern approach, 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*. In this course, we use the simpler system described in this paragraph.

[For comparison, 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 2.2.2.1 lists the elements that use the common system, along with their respective cation names. For example, Fe^{2+} is called the ferrous ion, while Fe^{3+} is called the ferric ion. In this course, we use the simpler system described in the previous paragraph.]

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 2.2.2.2 lists the names of some common monatomic ions.

Table 2.2.2.2: Some Monatomic Anions

Ion	Name
F^-	fluoride ion
Cl^-	chloride ion
Br^-	bromide ion
I^-	iodide ion
O^{2-}	oxide ion
S^{2-}	sulfide ion
P^{3-}	phosphide ion
N^{3-}	nitride ion

The polyatomic ions have their own characteristic names, as discussed earlier.

✓ Example 2.2.2.1

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 2.2.2.2)

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 2.2.2.1

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 2.2.2.2

Write the formula for each ion.

- a. the bromide ion
- b. the phosphate ion

- c. the cupric ion
- d. the magnesium ion

Answer a



Answer b



Answer c



Answer d



? Exercise 2.2.2.2

Write the formula for each ion.

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

Answer a



Answer b



Answer c

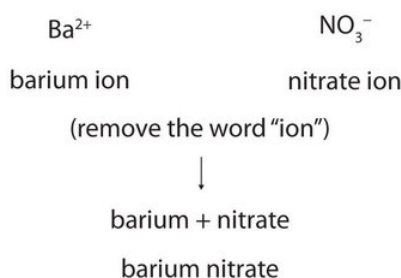


Answer d



Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. That's it: **we list cation then anion**. For example, what is the name of the compound whose formula is $\text{Ba}(\text{NO}_3)_2$?



The compound's name does not indicate that there are two nitrate ions for every barium ion. You must determine the relative numbers of ions by balancing the positive and negative charges.

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider FeCl_2 and FeCl_3 . In the first compound, the

iron ion has a 2+ charge because there are two Cl^- ions in the formula (1- charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride. If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively.

✓ Example 2.2.2.3

Name each ionic compound, using the common naming system.

- a. $\text{Ca}_3(\text{PO}_4)_2$
- b. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- 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

Answer e

tin(II) fluoride

? Exercise 2.2.2.3

Name each ionic compound, using the common system.

- a. ZnBr_2
- b. $\text{Fe}(\text{NO}_3)_3$
- c. Al_2O_3
- d. CuF_2
- e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride

Answer e

silver fluoride

Figure 2.2.2.1 is a synopsis of how to name simple ionic compounds.

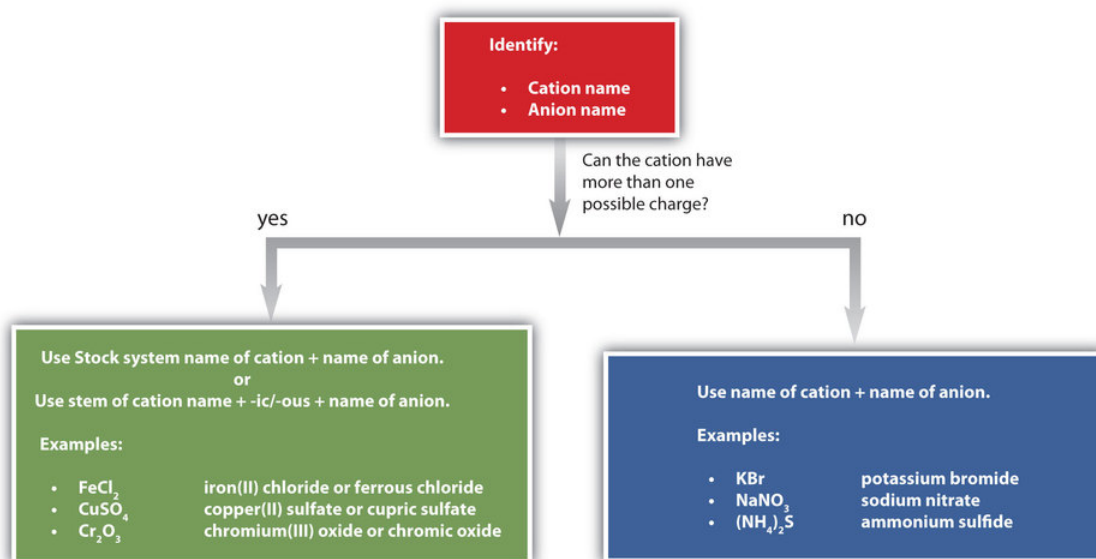


Figure 2.2.2.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

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 FeCl_2 , which is iron(II) chloride or ferrous chloride, CuSO_4 , which is copper(II) sulfate or cupric sulfate, and Cr_2O_3 , 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, NaNO_3 , which is sodium nitrate, and $(\text{NH}_4)_2\text{S}$, which is ammonium sulfide.

KEY TAKEAWAY

- Each ionic compound has its own unique name that comes from the names of the ions.

EXERCISES

- Briefly describe the process for naming an ionic compound.
- In what order do the names of ions appear in the names of ionic compounds?
- Which ionic compounds can be named using two different systems? Give an example.
- Name each ion.
 - Ra^{2+}
 - P^{3-}
 - H_2PO_4^-
 - Sn^{4+}
- Name each ion.
 - Cs^+
 - As^{3-}
 - HSO_4^-
 - Sn^{2+}
- Name the ionic compound formed by each pair of ions.
 - Na^+ and Br^-
 - Mg^{2+} and Br^-
 - Mg^{2+} and S^{2-}
- Name the ionic compound formed by each pair of ions.
 - K^+ and Cl^-
 - Mg^{2+} and Cl^-

c. Mg^{2+} and Se^{2-}

8. Name the ionic compound formed by each pair of ions.

- a. Na^+ and N^{3-}
- b. Mg^{2+} and N^{3-}
- c. Al^{3+} and S^{2-}

9. Name the ionic compound formed by each pair of ions.

- a. Li^+ and N^{3-}
- b. Mg^{2+} and P^{3-}
- c. Li^+ and P^{3-}

10. Name the ionic compound formed by each pair of ions.

- a. Fe^{3+} and Br^-
- b. Fe^{2+} and Br^-
- c. Au^{3+} and S^{2-}
- d. Au^+ and S^{2-}

11. Name the ionic compound formed by each pair of ions.

- a. Cr^{3+} and O^{2-}
- b. Cr^{2+} and O^{2-}
- c. Pb^{2+} and Cl^-
- d. Pb^{4+} and Cl^-

12. Name the ionic compound formed by each pair of ions.

- a. Cr^{3+} and NO_3^-
- b. Fe^{2+} and PO_4^{3-}
- c. Ca^{2+} and CrO_4^{2-}
- d. Al^{3+} and OH^-

13. Name the ionic compound formed by each pair of ions.

- a. NH_4^+ and NO_3^-
- b. K^+ and $\text{Cr}_2\text{O}_7^{2-}$
- c. Cu^+ and CO_3^{2-}
- d. Na^+ and HCO_3^-

14. Give two names for each compound.

- a. $\text{Al}(\text{HSO}_4)_3$
- b. $\text{Mg}(\text{HSO}_4)_2$

15. Give two names for each compound.

- a. $\text{Co}(\text{HCO}_3)_2$
- b. LiHCO_3

Answers

1. Name the cation and then the anion but don't use numerical prefixes.
2. the cation name followed by the anion name
3. Ionic compounds in which the cation can have more than one possible charge have two naming systems. FeCl_3 is either iron(III) chloride or ferric chloride (answers will vary).
4.
 - a. the radium ion
 - b. the phosphide ion
 - c. the dihydrogen phosphate ion
 - d. the tin(IV) ion or the stannic ion

5.
 - a. the cesium ion
 - b. the arsenide ion
 - c. the hydrogen sulfate ion
 - d. the tin(II) ion or the stannous ion
6.
 - a. sodium bromide
 - b. magnesium bromide
 - c. magnesium sulfide
7.
 - a. potassium chloride
 - b. magnesium chloride
 - c. magnesium selenide
8.
 - a. sodium nitride
 - b. magnesium nitride
 - c. aluminum sulfide
9.
 - a. lithium nitride
 - b. magnesium phosphide
 - c. lithium phosphide
10.
 - a. iron(III) bromide
 - b. iron(II) bromide
 - c. gold(III) sulfide
 - d. gold(I) sulfide
11.
 - a. chromium(III) oxide
 - b. chromium(II) oxide
 - c. lead(II) chloride
 - d. lead(IV) chloride
12.
 - a. chromium(III) nitrate
 - b. iron(II) phosphate
 - c. calcium chromate
 - d. aluminum hydroxide
13.
 - a. ammonium nitrate
 - b. potassium dichromate
 - c. copper(I) carbonate
 - d. sodium hydrogen carbonate or sodium bicarbonate
14.
 - a. aluminum hydrogen sulfate or aluminum bisulfate
 - b. magnesium hydrogen sulfate or magnesium bisulfate
- 15.

- a. cobalt hydrogen carbonate or cobalt bicarbonate
- b. lithium hydrogen carbonate or lithium bicarbonate

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2.2.3: Characteristics of Ionic Compounds

Learning Objectives

- To describe the 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 3.6.1: 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, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. (D) Vanadinite - the primary ore of vanadium, $\text{Pb}_3(\text{VO}_4)_3\text{Cl}$.

Physical Properties of Ionic Compounds

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°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 of table salt 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.

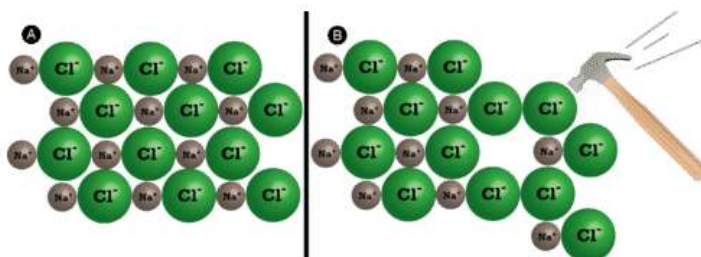


Figure 3.6.2: (A) The sodium chloride crystal (table salt) is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.

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.

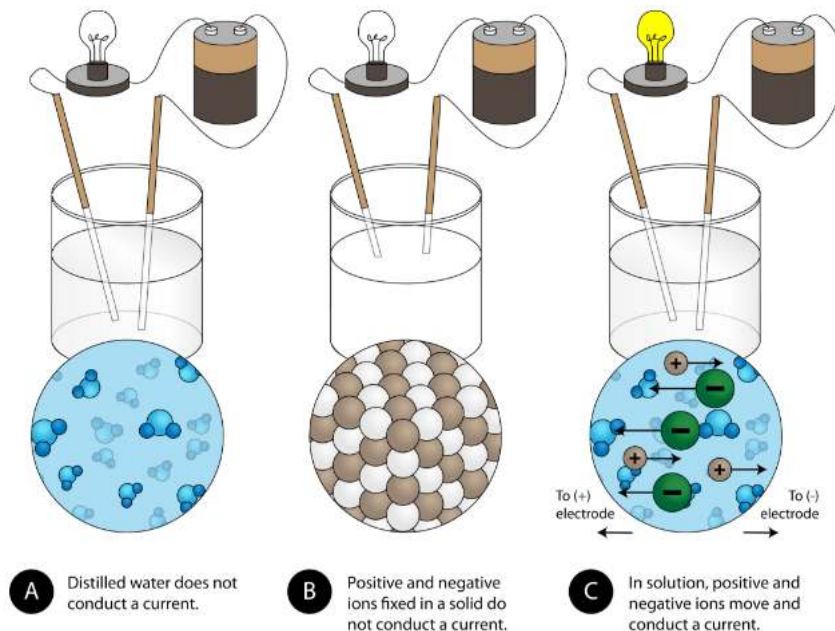


Figure 3.6.3: (A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.

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. Cations move to one electrode, while anions move to the other, allowing electricity to flow (see figure below). Melting an ionic compound also frees the ions to conduct a current. Ionic compounds conduct an electric current when melted or dissolved in water. The dissolution of ionic compounds in water will be discussed in Section 9.3.

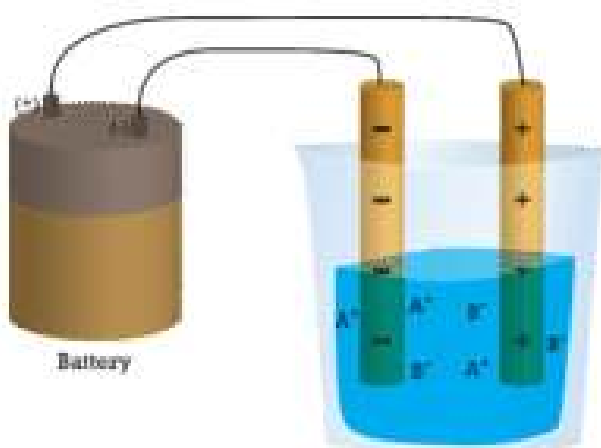
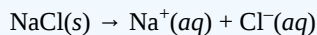


Figure 3.6.4: In an ionic solution, the A⁺ ions migrate toward the negative electrode, while the B⁻ ions migrate toward the positive electrode.

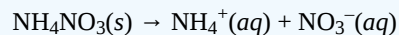
✓ Example 2.2.3.1

Write the equation that shows the separation of cations and anions when solid NaCl is dissolved in water.

Solution

ise

Write the equation that shows the separation of cations and anions when solid NH_4NO_3 is dissolved in water.

Answer

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.

Exercises

1. Explain how the bonding in an ionic solid explains some of the properties of these solids.
2. Which type(s) of solid conduct(s) electricity in their liquid state but not in their solid state?
3. Based on chemical formula, identify which of the following is an ionic solid?
 - a. Hg
 - b. PH_3
 - c. $\text{Ba}(\text{NO}_3)_2$

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3: Covalent Bonds

Learning Objectives

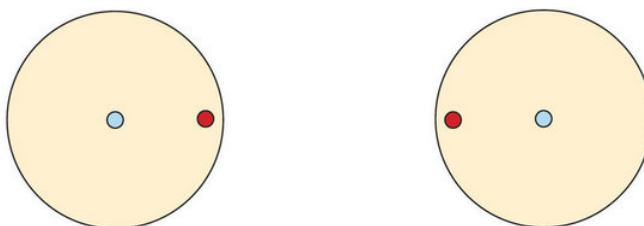
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H_2O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

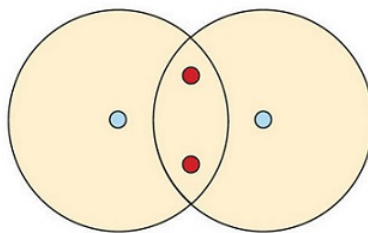
Electron Sharing

Previously, we discussed [ionic bonding](#) where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

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



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



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:



Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

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; $1 \text{ pm} = 1 \times 10^{-12} \text{ m}$). This particular bond length represents 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. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

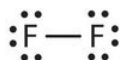


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



Two F's with two dots in between them, and two dots on the top, left/right side, and bottoms of each F.

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

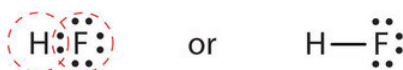
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

✓ Example 3.1

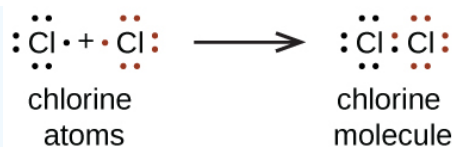
Use Lewis diagrams to indicate the formation of the following:

- Cl_2
- HBr

Solution

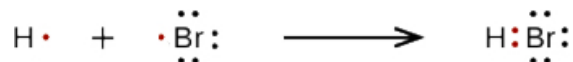
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.



H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

? Exercise 3.1

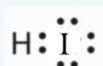
Draw the Lewis diagram for each compound.

- a molecule composed of one chlorine atom and one fluorine atom
- a molecule composed of one hydrogen atom and one iodine atom

Answer a:

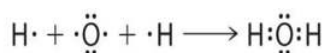


Answer b:



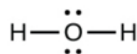
Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).



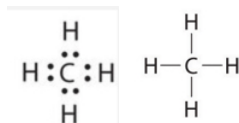
H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and two dots on bottom.

The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O . With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



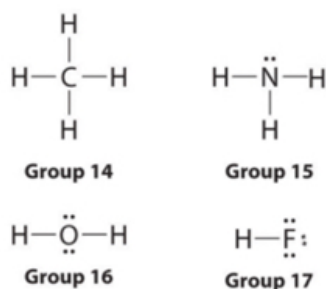
Water

Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis structures below. Again, sharing electrons between C and H atoms results in C achieving an octet while H achieving a duet number of electrons.



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). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (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 CH₄ (methane). **Group 5A** (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 NH₃ (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. 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.

This table shows atoms and their group numbers, and how many bonds and lone pairs each has.

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule**. Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure 3.1 shows the number of covalent bonds various atoms typically form.

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.

✓ Example 3.2

$$\begin{array}{c} \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\text{F} & -\text{O}- & \text{F}\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \end{array}$$

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.

$$\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{—}\ddot{\text{N}}\text{—}\ddot{\text{Cl}}\text{:} \\ | \\ \text{:}\ddot{\text{Cl}}\text{:} \end{array}$$

5

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3.1: Characteristics of Covalent Bonds

Learning Objectives

- Recognize bond characteristics of covalent compounds: bond length and bond polarity.
- Use electronegativity values to predict bond polarity.

Bond Length

The covalent bond in the hydrogen molecule (H_2) has a certain length (about $7.4 \times 10^{-11} \text{ m}$). Other covalent bonds also have known bond lengths, which are dependent on both the identities of the atoms in the bond and whether the bonds are single, double, or triple bonds. Table 3.1.1 lists the approximate bond lengths for some single covalent bonds. The exact bond length may vary depending on the identity of the molecule but will be close to the value given in the table.

Table 3.1.1: Approximate Bond Lengths of Some Single Bonds

Bond	Length ($\times 10^{-12} \text{ m}$)
H-H	74
H-C	110
H-N	100
H-O	97
H-I	161
C-C	154
C-N	147
C-O	143
N-N	145
O-O	145

Table 3.1.2 compares the lengths of single covalent bonds with those of double and triple bonds between the same atoms. Without exception, as the number of covalent bonds between two atoms increases, the bond length decreases. With more electrons between the two nuclei, the nuclei can get closer together before the internuclear repulsion is strong enough to balance the attraction.

Table 3.1.2: Comparison of Bond Lengths for Single and Multiple Bonds

Bond	Length ($\times 10^{-12} \text{ m}$)
C-C	154
C=C	134
C $\equiv$ C	120
C-N	147
C=N	128
C $\equiv$ N	116
C-O	143
C=O	120
C $\equiv$ O	113
N-N	145

Bond	Length ($\times 10^{-12} \text{ m}$)
N=N	123
N≡N	110
O–O	145
O=O	121

Electronegativity and Bond Polarity

Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, as in H_2 , there will always be one atom that attracts the electrons in the bond more strongly than the other atom does, as in HCl , shown in Figure 3.1.1. A covalent bond that has an equal sharing of electrons (Figure 3.1.1a) is called a **nonpolar covalent bond**. A covalent bond that has an unequal sharing of electrons, as in Figure 3.1.1b is called a **polar covalent bond**.

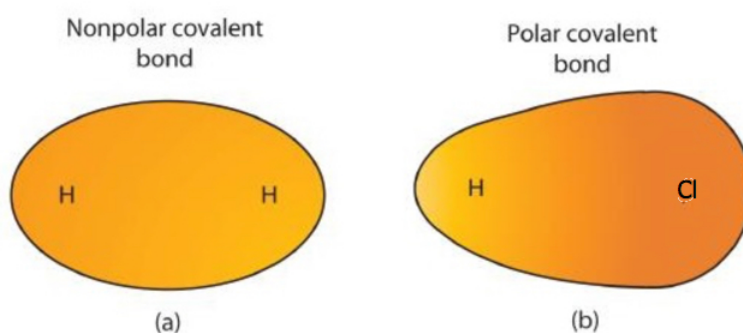


Figure 3.1.1 Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The chlorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

The distribution of electron density in a polar bond is uneven. It is greater around the atom that attracts the electrons more than the other. For example, the electrons in the $\text{H}-\text{Cl}$ 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 3.1.1b 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). This is seen in Figure 3.1.2a. The separation of charge in a polar covalent bond results in an electric dipole (two poles), represented by the arrow in Figure 3.1.2b. The direction of the arrow is pointed toward the δ^- end while the $+$ tail of the arrow indicates the δ^+ end of the bond.

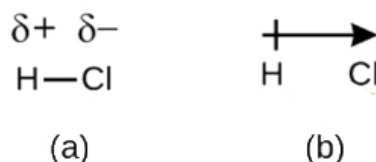


Figure 3.1.2: (a) Unequal sharing of the bonding pair of electrons between H and Cl leads to partial positive charge on the H atom and partial negative charge on the Cl . Symbols δ^+ and δ^- indicate the polarity of the $\text{H}-\text{Cl}$ bond. (b) The dipole is represented by an arrow with a cross at the tail. The cross is near the δ^+ end and the arrowhead coincides with the δ^- .

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. There are various numerical scales for rating electronegativity. Figure 3.1.3 shows one of the most popular—the Pauling scale.

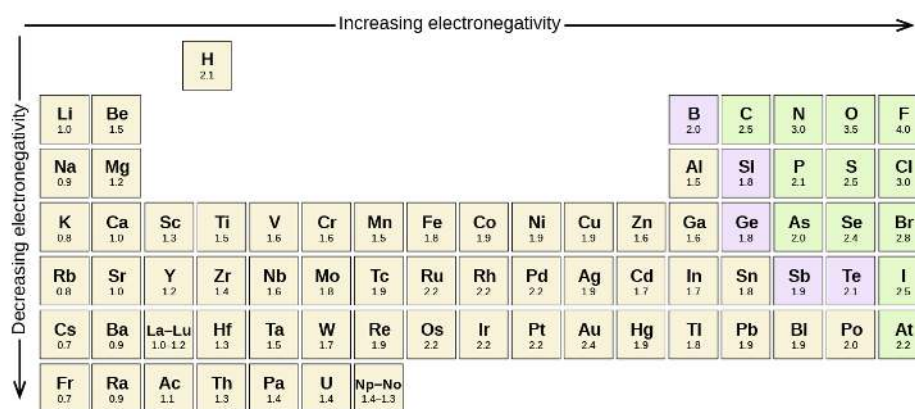
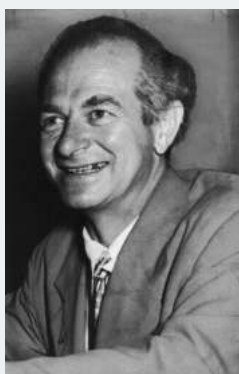


Figure 3.1.3 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).

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.

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 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**.

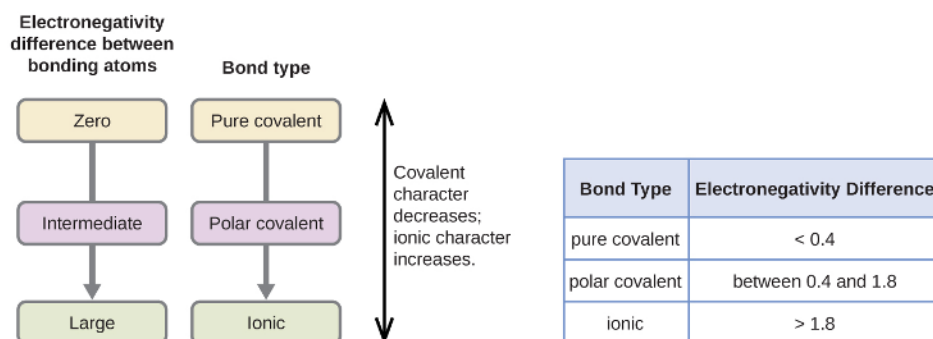


Figure 3.1.4: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

✓ Example 3.1.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

- C and H
- H and H
- Na and Cl
- O and H

Solution

- 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.
- Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
- 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.
- 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 3.1.1

Describe the electronegativity (EN) difference between each pair of atoms and the resulting polarity (or bond type).

- C and O
- K and Br
- N and N
- 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.

Bond Polarity and Molecular 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**. A **polar molecule** is a molecule in which 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 is called a **dipole**. A simplified way to depict polar molecules like HF is pictured below (see figure below).



Figure 3.1.5: A molecular dipole results from the unequal distribution of electron density throughout a molecule.

When placed between oppositely charged plates, polar molecules orient themselves so that their positive ends are closer to the negative plate and their negative ends are closer to the positive plate (see Figure 4.4.6 below).

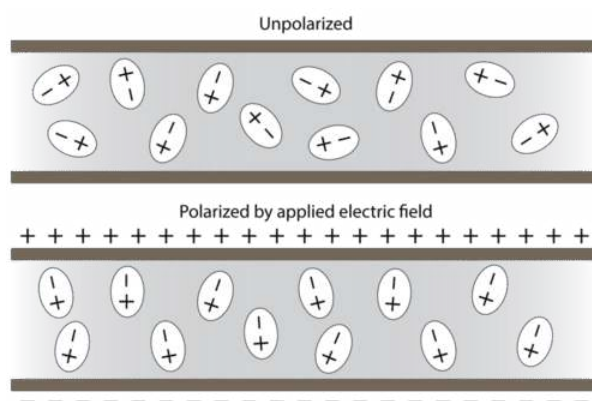


Figure 3.1.6: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves to maximize the attraction between opposite charges (bottom).

Experimental techniques involving electric fields can be used to determine if a certain substance is composed of polar molecules and to measure the degree of polarity.

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. (Figure 3.1.7) is a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a **linear** molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented directly opposite each other, they cancel each other out, and the overall molecular polarity of CO_2 is zero. CO_2 is a **nonpolar** molecule. In H_2O , the orientation of the two O–H bonds is **bent**: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule itself is **polar**. The polarity of water has an enormous impact on its physical and chemical properties. For example, the boiling point of water (100°C) is high for such a small molecule due to the fact that polar molecules attract each other strongly. On the other hand, the nonpolar carbon dioxide becomes a gas at -77°C , almost 200° lower than the temperature at which water boils. More details will be presented in the next section.



Figure 3.1.7 Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.

Key Takeaways

- Covalent bonds between different atoms have different bond lengths.
- Covalent bonds can be polar or nonpolar, depending on the electronegativity difference between the atoms involved.

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3.2: Covalent Compounds - Formulas and Names

Learning Objectives

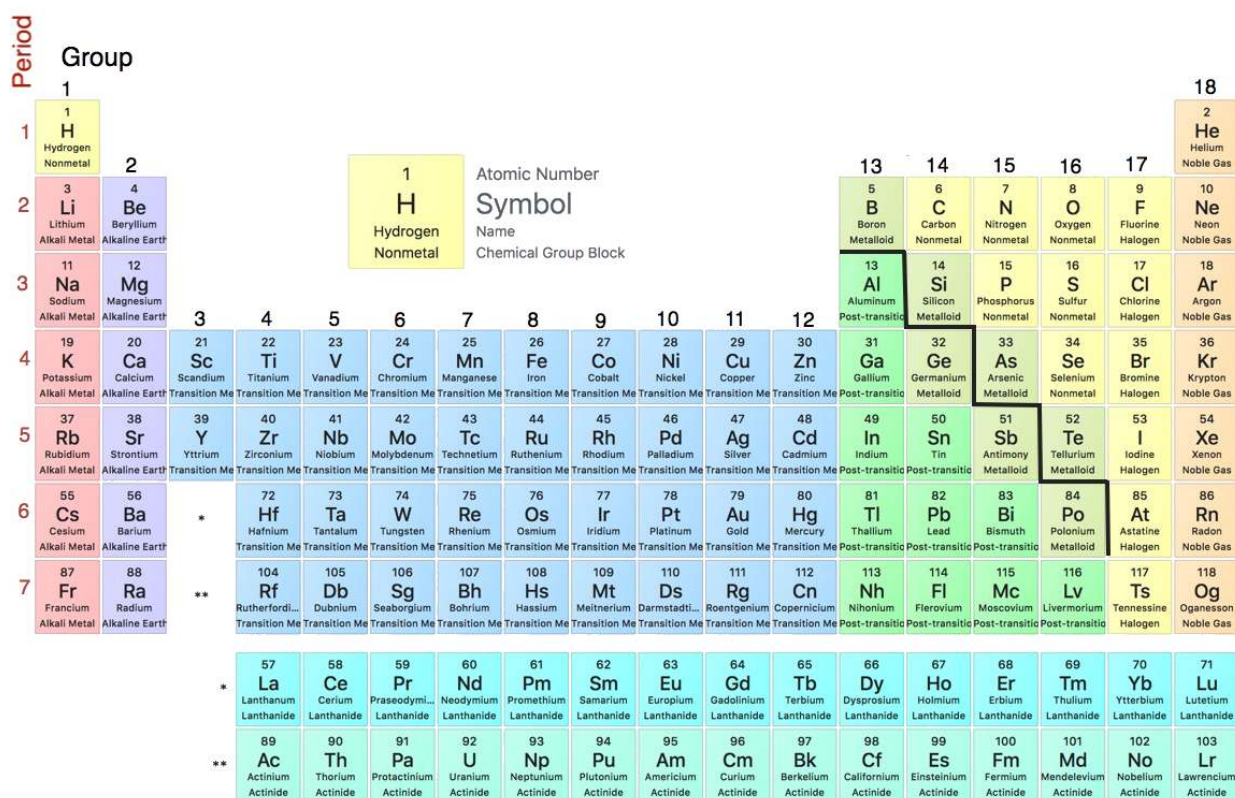
- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

COVALENT AND IONIC COMPOUNDS

Which elements make covalent bonds? Covalent bonds form when *two or more nonmetals combine*. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds.

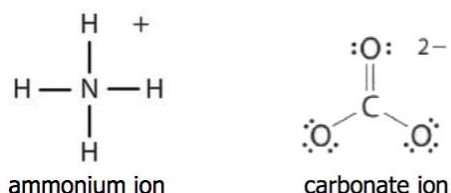
As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic: sodium is a metal and chlorine is a non-metal. Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide (SiO₂) will be a covalently bound molecule (a semi-metal and a non-metal) and MgCl₂ will be ionic (a metal and a non-metal).

Reminder: one can identify whether an element is a metal or a nonmetal by looking at the periodic table. All elements to the left of the black stairstep divider are metals; only those few elements to the right of the divider are nonmetals.



Period	Group	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-transition	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 Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-transition	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 Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-transition	50 Sn Tin Post-transition	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 Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-transition	82 Pb Lead Post-transition	83 Bi Bismuth Post-transition	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 Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-transition	114 Fl Flerovium Post-transition	115 Mc Moscovium Post-transition	116 Lv Livermorium Post-transition	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
				*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium 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

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of NH₄⁺. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2-. The formula of the carbonate ion is CO₃²⁻.



The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.1. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride (NH_4Cl) has ionic bonding between a polyatomic ion, NH_4^+ , and Cl^- ions, but within the ammonium ion (NH_4^+), the nitrogen and hydrogen atoms are connected by covalent bonds (shown above).

Both ionic and covalent bonding are also found in calcium carbonate. Calcium carbonate (CaCO_3) has ionic bonding between calcium ion Ca^{2+} and a polyatomic ion, CO_3^{2-} , but within the carbonate ion (CO_3^{2-}), the carbon and oxygen atoms are connected by covalent bonds (shown above).

Characteristics of Covalent (Molecular) Compounds

Compounds that contain covalent bonds (also called molecular compounds) exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds (discussed in Section 3.6). For example, water (molecular compound) boils at 100°C while sodium chloride (ionic compound) boils at 1413°C . In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state. The attraction between molecules (called intermolecular forces) will be discussed in more detail in Section 8.1

✓ Example 3.2.1

Is each compound formed from ionic bonds, covalent bonds, or both?

- Na_2O
- Na_3PO_4
- N_2O_4

Answer a

The elements in Na_2O are a metal and a nonmetal, which form ionic bonds.

Answer b

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, within the polyatomic phosphate ion, the atoms are held together by covalent bonds, so this compound contains both ionic and covalent bonds.

Answer c

The elements in N_2O_4 are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

? Exercise 3.2.1

Is each compound are formed from ionic bonds, covalent bonds, or both?

- $\text{Ba}(\text{OH})_2$
- F_2
- PCl_3

Answer a:

both

Answer b:

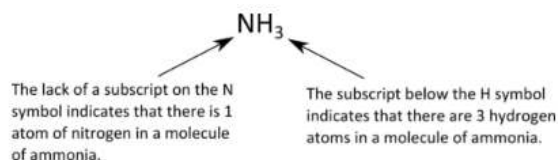
covalent

Answer c:

covalent

MOLECULAR FORMULAS

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first (H_2O is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen CH_4 , the molecular formula for methane. Below is the molecular formula of ammonia, NH_3 .



NH_3 . An arrow points to the N and says, "The lack of a subscript on the N symbol indicates that there is 1 atom of nitrogen in a molecule of ammonia". An arrow points to H and says, "The subscript below the H symbol indicates that there are 3 hydrogen atoms in a molecule of ammonia".

NAMING COVALENT COMPOUNDS

While naming compounds is beyond the scope of the class, it's helpful to note that compound names are derived by a system. Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 3.2.1 lists these numerical prefixes. 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").

For example, consider the compound whose molecular formula is CCl_4 . The name begins with the name of the first element—carbon. The second element, *chlorine*, becomes *chloride*, 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.

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 in a separate section.

Key Takeaways

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

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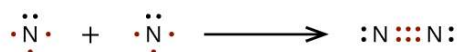
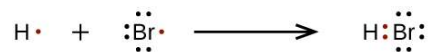
3.3: Drawing Lewis Structures

Learning Objectives

- To draw Lewis structures.
- To recognize molecules that are likely to have multiple covalent bonds.

DRAWING LEWIS STRUCTURES

For very simple molecules and molecular ions, we can visualize the distribution of electrons involved in bonds by writing a Lewis structure. We can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:

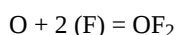


For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

- Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
- Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
- Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
- Place all remaining electrons on the central atom.
- Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of OF_2 and HCN as examples in following this procedure:

- Determine the total number of valence (outer shell) electrons in the molecule or ion. For a molecule, we add the number of valence electrons (use the main group number) on each atom in the molecule. This is the total number of electrons that must be used in the Lewis structure.



$$6e^- + (2 \times 7e^-) = 20e^-$$



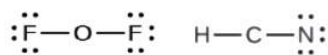
$$1e^- + 4e^- + 5e^- = 10e^-$$

- Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. Note that H and F can only form one bond, and are always on the periphery rather than the central atom.



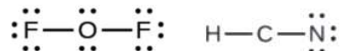
- Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- In OF_2 , six electrons are placed on each F.
- In HCN , six electrons placed on N



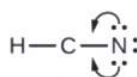
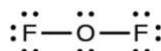
4. Place all remaining electrons on the central atom.

- In OF_2 , 4 electrons are placed on O.
- In HCN : no electrons remain (the total valence of $10e^-$ is reached) so nothing changes.



5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

- In OF_2 , each atom has an octet as drawn, so nothing changes.
- In HCN , form two more C–N bonds



gives

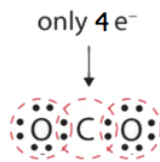


H dash C dash N with 6 dots around the N. 4 of the dots are pointing to the dash connecting the C and the N. This turns the formula into H dash C and three lines connecting the C and N together, with two dots on the outside of the N.

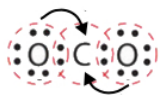
Finally, check to see if the total number of valence electrons are present in the Lewis structure. And then, inspect if the H atom has 2 electrons surrounding it and if each of the main group atoms is surrounded by 8 electrons.

MULTIPLE BONDS

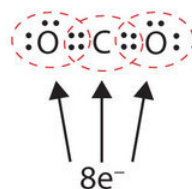
In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons. Review HCN in Step 5 above. Another example is carbon dioxide (CO_2). CO_2 has a total valence of $4e^- + (2 \times 6e^-) = 16e^-$. Following steps 1 to 4, we draw the following:



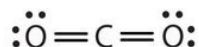
This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared electrons is far from satisfactory.



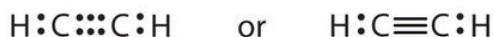
In this case, more than one pair of electrons must be shared between two atoms for both atoms to have an octet. A second electron pair from each oxygen atom must be shared with the central carbon atom shown by the arrows above. A lone pair from each O must be converted into a bonding pair of electrons.



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:



Some molecules contain triple bonds (like HCN, shown above). Triple bonds are covalent bonds in which *three* pairs of electrons are shared by two atoms. Another compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:



✓ Example 3.3.1

Draw the Lewis diagram for each molecule.

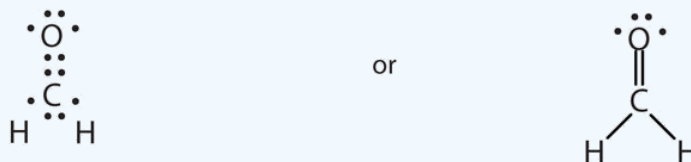
1. N_2
2. CH_2O (The carbon atom is the central atom.) One application of CH_2O , also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.

Solution

1. The total number of electrons is $2 \times 5 = 10$ electrons. The bond between the two nitrogen atoms is a triple bond. The Lewis diagram for N_2 is as follows:



2. The total number of electrons is $4 \times 2(1) + 6 = 12$ electrons. In CH_2O , the central atom is surrounded by two different types of atoms. The Lewis diagram that fills each atom's valence electron shell is as follows:

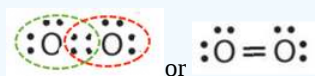


? Exercise 3.3.1

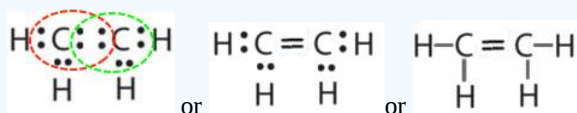
Draw the Lewis diagram for each molecule.

- a. O_2
- b. C_2H_4

Answer a:

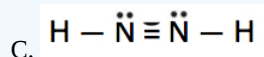
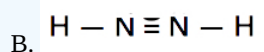
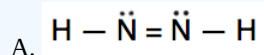


Answer b:



✓ Example 3.3.2

Which is the correct Lewis structure for N_2H_2 ?



Solution

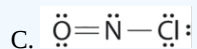
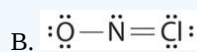
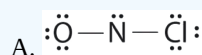
Lewis structure A is the correct answer. It has a total of $(2 \times 5e^-) + (2 \times 1e^-) = 12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

Structure B is electron deficient. It has only $10e^-$ instead of 12.

Structure C has 14 (2 extra) electrons. The N atoms do not satisfy the octet.

Exercise

Which is the correct Lewis structure for NOCl?



Answer

Structure A violates the octet rule; N is surrounded by only $6e^-$.

Structure B violates the octet rule; Cl has $10e^-$ around it. Furthermore, there are a total of $20e^-$ instead of $18e^-$.

Structure C is the correct structure. It has a total of $6e^- + 5e^- + 7e^- = 18e^-$. Each atom is surrounded by 8 electrons (octet rule).

Key Takeaways

- A Lewis structure shows the bonding and nonbonding electrons around individual atoms in a molecule.
- Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.
- A double bond contains four electrons and a triple bond contains six electrons.

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3.3.1: Characteristics of Molecules - Shape and Polarity

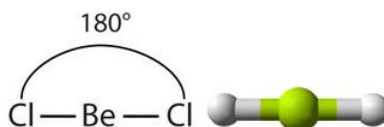
Learning Objectives

- Predict the general shape of a simple covalent molecule.
- Predict the polarity of the molecule.
- Compare the properties of ionic and molecular compounds.

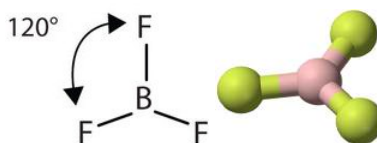
Unlike the ions in ionic compounds, which are arranged in lattices called crystals, molecules of covalent compounds exist as discrete units with a characteristic three-dimensional shape.

Molecular Shape: VSEPR Theory

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the **valence shell electron pair repulsion (VSEPR) theory**. For example, the two covalent bonds in BeCl_2 **stay as far from each other** as possible, ending up 180° apart from each other. The result is a **linear** molecule:



The three covalent bonds in BF_3 repel each other to form 120° angles in a plane, in a shape called **trigonal planar**:



The molecules BeCl_2 and BF_3 actually **violate the octet rule**; however, such exceptions are rare and will not be discussed in this text.

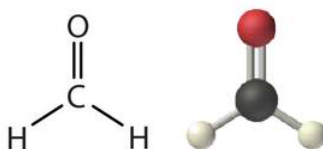
Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your “bonds” are farther apart than the planar 120° orientation.

The four covalent bonds in CCl_4 arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5° . CCl_4 is said to have a **tetrahedral** shape:

Table describes how to use the number of atoms around the central atom to determine the geometry of a molecule, as well as examples.

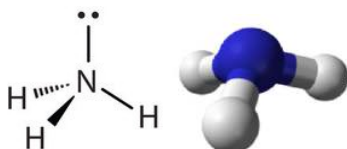
Atoms Around Central Atom	Geometry	Example
2 AB_2	Linear	BeCl_2
3 AB_3	Trigonal Planar	BF_3
4 AB_4	Tetrahedral	CCl_4

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with multiple bonds are determined by treating the multiple bonds as one bond. Thus, formaldehyde (CH_2O) has a shape similar to that of BF_3 . It is **trigonal planar**.

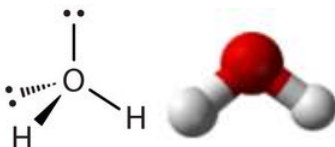


Molecules With Lone Pairs Around Central Atom

Molecules with lone electron pairs around the central atom have a shape based on the position of the atoms, not the electron pairs. For example, NH_3 has **one lone electron pair** and **three bonded electron pairs**. These four electron pairs repel each other and adopt a tetrahedral arrangement. However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, NH_3 is said to have a **trigonal pyramidal** shape, not a tetrahedral one.



Similarly, H_2O has **two lone pairs** of electrons around the central oxygen atom and **two bonded electron pairs**. Although the four electron pairs adopt a tetrahedral arrangement, the shape of the molecule is described by the positions of the atoms only. The shape of H_2O is **bent** with an approximate 109.5° angle.



In summary, to determine the molecular geometry:

Step 1: Draw the Lewis structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the **central atom**.

Step 3: Use Table 4.5.1 to determine the molecular geometry.

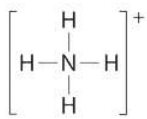
Number of bonds and lone pairs	Number of bonds 0 lone pair	1 lone pair	2 lone pairs
2	 Linear		
3	 Trigonal planar	 Bent or angular	
4	 Tetrahedral	 Trigonal pyramidal	
			 Bent or angular

If a molecule has 2 bonds and 0 lone pairs, it is linear. If a molecule has 3 bonds and 0 lone pairs, it is trigonal planar. If a molecule has 3 bonds and 1 lone pair, it is bent or angular. If a molecule has 4 bonds and 0 lone pairs, it is tetrahedral. If a molecule has 4 bonds and 1 lone pair, it is trigonal pyramidal. If a molecule has 4 bonds and 2 lone pairs, it is bent or angular.

Table 4.5.1: The molecular geometry depends on the number of bonds and lone pairs around the **central atom, A**.

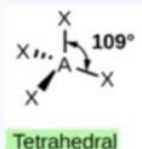
✓ Example 3.3.1.1

What is the geometry of the ammonium ion, NH_4^+ ? Its Lewis structure is shown below. How is this different from ammonia, NH_3 ?

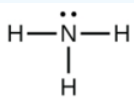


Solution

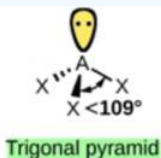
In ammonium ion, the central atom N has 4 bonds and no lone pair. It is equivalent to the below in Table 4.5.1. Hence, this is *tetrahedral*.



In ammonia (NH_3), shown below, N has 3 bonds and one lone pair.

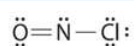


It is equivalent to the below in Table 4.5.1. Hence, the shape of this molecule is *trigonal pyramid*.



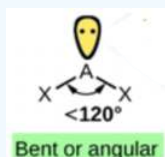
ise

What is the molecular shape of nitrosyl chloride, a highly corrosive, reddish-orange gas? Its Lewis structure is shown below.



Answer

Focus on the central atom, N. It has a double bond to O, count this as one bond. It also has a single bond to Cl. Thus, N has 2 bonds and one lone pair. These 3 electron pairs will spread out 120 degrees from each other. But, since the shape is defined by the arrangement of the atoms only, the shape is bent or angular. If you consult Table 4.5.1, this molecule is equivalent to the below. Hence, two bonds and one lone pair has a *bent or angular* shape.



Molecular Polarity

In general, a molecule is nonpolar if all its bonds are nonpolar. Examples are I_2 , O_2 , H_2 , CH_4 , C_2H_6 and C_3H_8 .

In general, a molecule is polar if it contains polar bonds EXCEPT when the bond polarities cancel each other. As mentioned in Section 4.4, the shape of the CO_2 molecule (linear) orients the two $\text{C}=\text{O}$ polar bonds **directly opposite** each other, thus **cancelling** each other's effect. **Carbon dioxide** (CO_2) is a **nonpolar** molecule.

On the other hand, water (as discussed above) is a bent molecule because of the two lone pairs on the central oxygen atom. Because of the bent shape, the dipoles do not cancel each other out and the water molecule is **polar**. In the figure below, the individual $\text{H}-\text{O}$ polar bonds represented by the two red arrows are not directly opposite each other. These two dipoles don't cancel each other out. In fact, the net dipole (blue arrow) points upward. There is a resultant partial positive charge at one end (between the two H atoms) and a partial negative charge on the other end (where O is located). The uneven distribution of charge or the overall dipole is shown by the blue arrow below (Figure 4.5.1). Hence, **water is polar** (has + and - poles) while **carbon dioxide is nonpolar**.

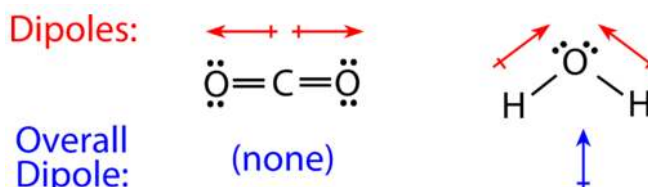


Figure 4.5.1: The molecular geometry of a molecule (linear vs. bent) affects its polarity.

Similarly, in BF_3 (trigonal planar), the effect of a $\text{B}-\text{F}$ bond is cancelled by the sum of the other two $\text{B}-\text{F}$ bonds (see video). Hence, a trigonal planar molecule (BF_3) is nonpolar because the bond polarities cancel each other, but a trigonal pyramidal molecule (NH_3) is polar.

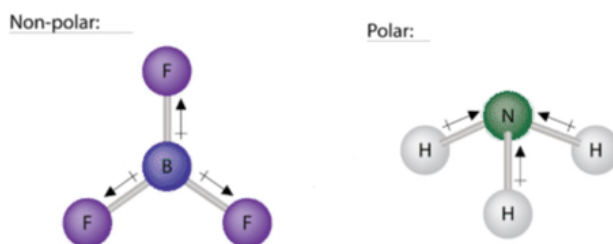


Figure 4.5.2: The molecular geometry of a molecule (trigonal planar vs. trigonal pyramid) affects its polarity.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CCl_4 is **nonpolar**. However, if the peripheral atoms are not of the same electronegativity, the bond polarities don't cancel and the molecule becomes **polar**, as in CH_3Cl .

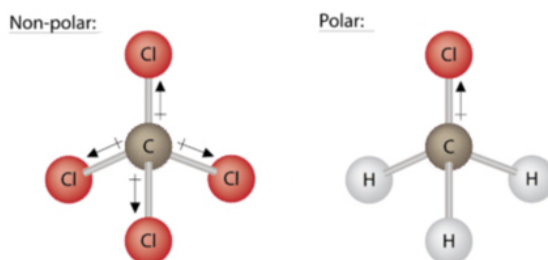


Figure 4.5.3: The same molecular geometry but peripheral bonds are of different electronegativity. CCl_4 is nonpolar but CH_3Cl is polar.

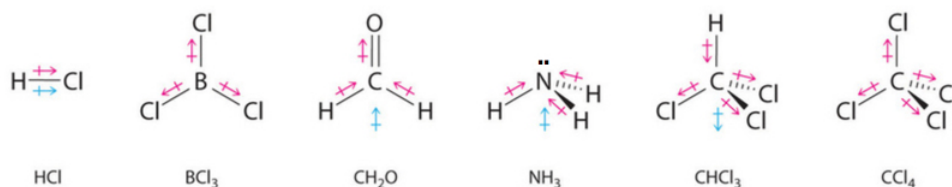


Figure 3.3.1.4: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole moment (HCl , CH_2O , NH_3 , and CHCl_3), indicated in blue, whereas others do not because the bond dipoles cancel due to symmetry (BCl_3 and CCl_4).

Physical Properties of 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 in Section 8.1) 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 4.5.2: 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.

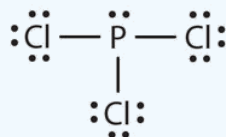
✓ Example 3.3.1.2

Describe the shape of each molecule. Is it polar or nonpolar?

- PCl_3
- CO_2

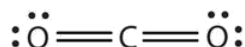
Solution

- The Lewis diagram for PCl_3 is as follows:



Focus on the central atom, P that has 3 bonds and one lone pair. The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like NH_3 , this molecule is *pyramidal*. The 3 P-Cl bonds don't cancel each other. This is *polar*.

- The Lewis diagram for CO_2 is as follows:



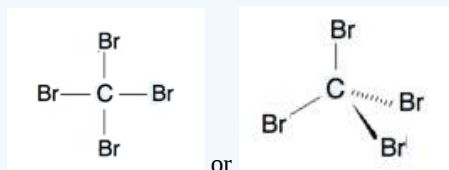
Focus on the central atom, C. The multiple bonds are treated as one group, hence C has 2 bonds and zero lone pair. CO₂ has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO₂ molecules are *linear*. This is highly symmetrical, with the two opposite dipoles cancelling each other. The CO₂ molecule is *nonpolar*.

? Exercise 3.3.1.2

Describe the shape of each molecule. Is it polar or nonpolar?

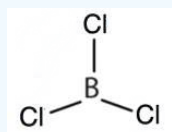
- CB₄
- BCl₃

Answer a:



The Lewis structure shows 4 groups attached to the central atom, hence *tetrahedral*. All the 4 groups are identical and the shape is symmetrical. Hence, it is *nonpolar*.

Answer b:



The Lewis diagram shows 3 groups attached to the central atom, hence *trigonal planar*. All the 3 groups are identical and shape is symmetrical, hence, it is *nonpolar*.

Key Takeaways

- A molecule has a certain mass, called the molecular mass.
- Simple molecules have geometries that can be determined from VSEPR theory.
- Polar molecules result from differences in electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

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3.4: Organic Compounds

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 3.4.1.

Table 3.4.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 3.4.1 also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C₆H₁₄), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 3.4.1.

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3.4.1: Structures and Names of Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

Consider below the three simplest alkanes—methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) and they are shown again in Figure 3.4.1.1. You can observe a pattern in the bonds drawn in these compounds: all carbon atoms have bonds to four other atoms, and every hydrogen atom forms a bond to one other atom. This bonding pattern is observed for carbon and hydrogen for all organic compounds.

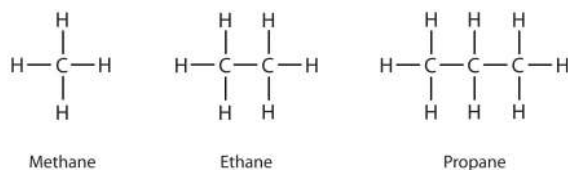


Figure 3.4.1.1: The Three Simplest Alkanes

Methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) 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 CH₂ unit. The first 10 members of this series are given in Table 3.4.1.1.

Table 3.4.1.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C _n H _{2n + 2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH ₄	CH ₄	—
ethane	C ₂ H ₆	CH ₃ CH ₃	—
propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃	—
butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	2
pentane	C ₅ H ₁₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	3
hexane	C ₆ H ₁₄	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	5
heptane	C ₇ H ₁₆	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	9
octane	C ₈ H ₁₈	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	18
nonane	C ₉ H ₂₀	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	35
decane	C ₁₀ H ₂₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	75

Consider the series in Figure 3.4.1.3 The sequence starts with C_3H_8 , and a CH_2 unit is added in each step moving up the series. The members of this series have properties that vary in a regular and predictable manner. This sequence demonstrates the principle of *homology* which gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

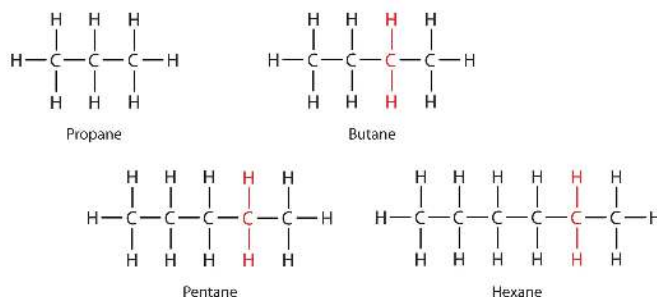


Figure 3.4.1.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2} . Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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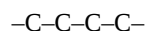
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3.4.2: Branched-Chain Alkanes

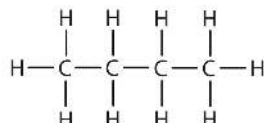
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

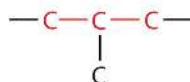
In the last section you considered a series of *straight-chain* hydrocarbons. But in accomplishing the goal of creating four bonds for each carbon atom, each carbon atom might be bonded to several other carbon atoms. For example, consider butane (C_4H_{10}). We can write the structure of butane by stringing four carbon atoms in a row,



and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

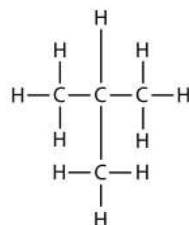


Figure 3.4.2.1).

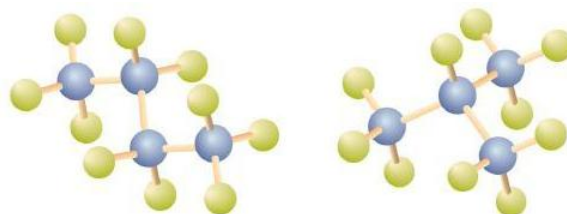
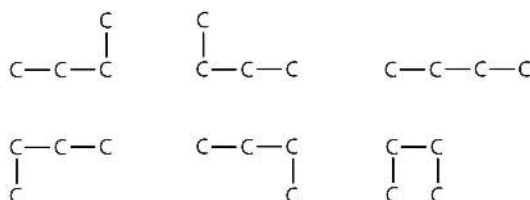


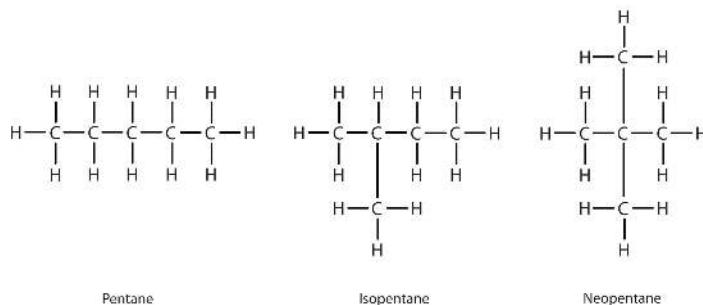
Figure 3.4.2.1: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10} .

Notice that C_4H_{10} is depicted with a bent chain in Figure 3.4.2.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure 3.4.2.1). Unlike C_4H_{10} , the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12} . (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning “new”). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, $36.1^\circ C$; isopentane, $27.7^\circ C$; and neopentane, $9.5^\circ C$.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

✓ Example 3.4.2.1

A student is asked to write structural formulas for two different hydrocarbons having the molecular formula C_5H_{12} . She writes one formula with all five carbon atoms in a horizontal line and the other with four carbon atoms in a line, with a $-CH_3$ group extending down from the first attached to the third carbon atom. Do these structural formulas represent different molecular formulas? Explain why or why not.

Answer

No; both are five-carbon continuous chains.

? Exercise 3.4.2.1

How many different isomers exist for the molecule C_4H_{10} ?

Answer

Two: the straight-chain butane, and one isomer with three carbons in a line, and a $-CH_3$ group branched off the central carbon atom.

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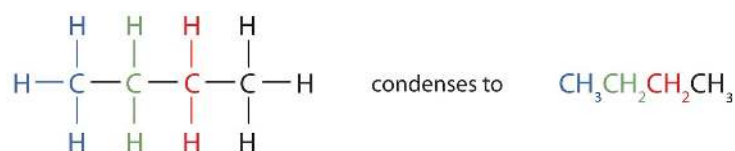
3.4.3: Condensed Structural and Line-Angle Formulas

Learning Objectives

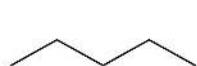
- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

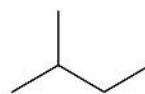
Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Pentane



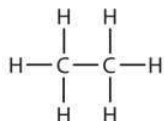
Isopentane

Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

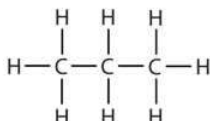
✓ Example 3.4.3.1

Write the condensed formula for each of the following structural formulas.

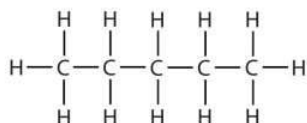
a.



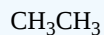
b.



c.



Answer a



Answer b



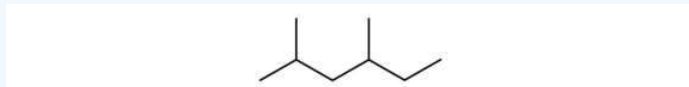
Answer c



? Exercise 3.4.3.1

Complete the following translations between complete structural formulas, condensed structural formulas, and line-angle formulas.

- A condensed structural formula for isohexane can be written as $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$. Draw the line-angle formula for isohexane.
- Draw the line-angle formula for the compound $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$.
- Give the structural formula for the compound represented by this line-angle formula:



Answer a

The longest chain should contain five carbon atoms in a row; the carbon atom on the end has a branch to another carbon.

Answer b

The longest chain should contain six carbon atoms in a row; the third carbon atom has a branch to another carbon.

Answer c



Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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CHAPTER OVERVIEW

4: Interactions Between Substances

[4.1: Heat and Temperature](#)

[4.2: Phase Changes](#)

[4.3: Intermolecular Interactions](#)

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4.1: Heat and Temperature

Learning Objectives

- To relate heat transfer to temperature change.
- Compare temperature systems for measurements in units of Celsius, Fahrenheit and Kelvin.
- Understand how body temperature can vary.

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

Temperature Scales

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. There are three scales used for reporting temperatures. Figure 4.1.1 compares the three temperature scales: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

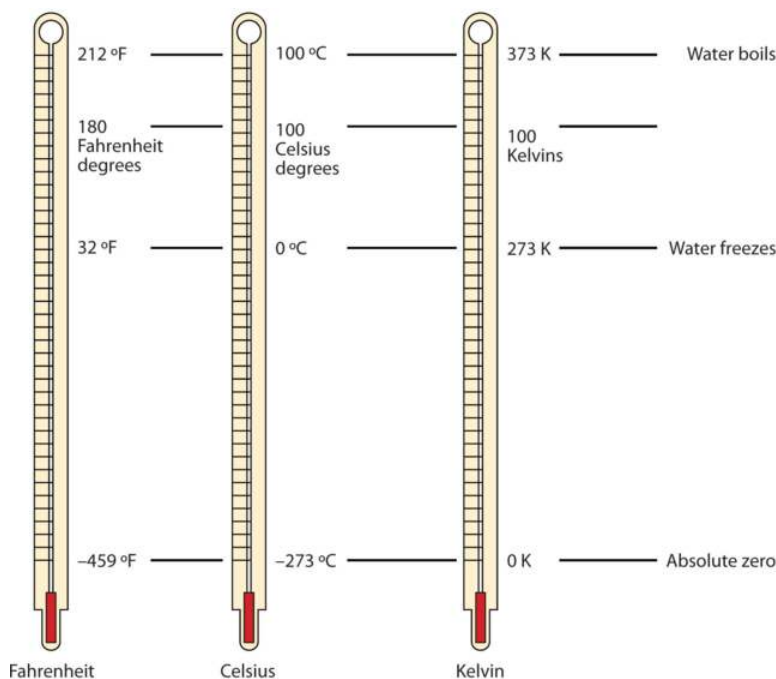


Figure 4.1.1: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver looking thermometers contain mercury, which is a neurotoxin.

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. For example, the Celsius scale (symbolized by °C and spoken as “degrees Celsius”) defines 0°C as the freezing point of water and 100 °C as the boiling point of water. This scale is divided into 100 divisions between these two landmarks and extended higher and lower as well. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \times \frac{5}{9} \quad (4.1.1)$$

$$^{\circ}\text{F} = \left(^{\circ}\text{C} \times \frac{9}{5}\right) + 32 \quad (4.1.2)$$

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.

In this course, you may encounter recipes and resources that use the Celsius scale. Look carefully at the temperature units associated with baking temperatures, and so forth. Most common digital thermometers are easily toggled between Fahrenheit and Celsius.

The fundamental unit of temperature 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:

$$\text{K} = ^{\circ}\text{C} + 273.15 \quad (4.1.3)$$

For most purposes, it is acceptable to use 273 instead of 273.15 in Equation 4.1.3.

Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as “two hundred ninety-five kelvin” and not “two hundred ninety-five degrees Kelvin.”

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

Health Application: Body temperature

Normal body temperature is defined as being 98.6°F (+/- 1.0°F). To determine body temperature, thermometers can be placed inside or on the surface of the body. The two best methods of obtaining body temperature are placing the thermometer either under the tongue or inside the rectum. Typically, children are capable of holding a thermometer in their mouths around the age of four (have fun before that age).

Fever is defined as body temperature being above 100°F (adults). High fever status occurs at and above 104°F. For adults, these adults should seek medical attention immediately if the fever exceeds 104°F. For children, these values are much lower.

Hyperthermia (inability of the body to regulate heat) occurs when normal body temperature is exceeded. Conditions that can cause hyperthermia are fever (infection), heat stroke, thyroid disorders, heart attack, or traumatic injury. Medications for cancer, arthritis, and thyroid patients can cause the body temperature to rise. Symptoms of hyperthermia include sweating, confusion, nausea, and dizziness.

Hypothermia (exposure to cold environments) occurs when normal body temperature dips below 95.0°F. When this occurs, the affected person(s) should seek immediate medical attention. During hypothermia, the body has problems producing heat. Medical conditions like diabetes, infection, and thyroid dysfunction can cause hypothermia. Watch this video of American Marines attempting to survive extreme environments. Symptoms of this condition involve shivering, confusion, and sluggish behavior.

Treating hyperthermia could involve hydrating a patient. If a fever is due to infection, analgesics (like Tylenol, Advil, aspirin, or Aleve) can help alleviate fever. Placing someone in a cool bath can also relieve symptoms.

To combat hypothermia, one must remove wet clothing, redress in warm materials, and participate in physical movement.

Summary

- Heat transfer is related to temperature change.
- Temperature is commonly measured in units of Celsius, Kelvin, and Fahrenheit.

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4.2: Phase Changes

Learning Objectives

- Determine the heat associated with a phase change.

Matter can exist in one of several different states, including a gas, liquid, or solid state. The amount of energy in molecules of matter determines the **state of matter**.

- A **gas** is a state of matter in which atoms or molecules have enough energy to move freely. The molecules come into contact with one another only when they randomly collide. For example, the water molecules within a bubble rising from a pot of boiling water are all in the gas phase. Carbon dioxide is a gas generated from the action of yeast on sugar when breads rise.
- A **liquid** is a state of matter in which atoms or molecules are constantly in contact but have enough energy to keep changing positions relative to one another. Of course, water is a common liquid used in cooking.
- A **solid** is a state of matter in which atoms or molecules do not have enough energy to move. They are constantly in contact and in fixed positions relative to one another. Frozen water, or ice, is an example of the solid state for water. Sugar crystals are another example of a pure solid.

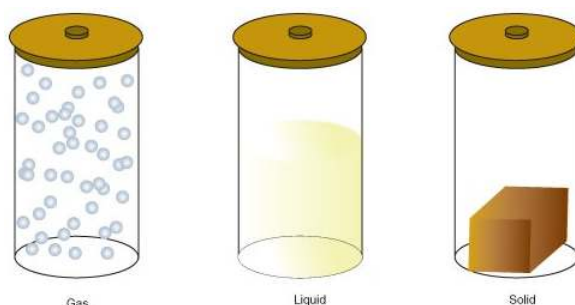


Figure 4.2.1: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, the substance is a liquid, which has spread to take the shape of its container but not the volume. In the right-hand container, the substance is a solid, which takes neither the shape nor the volume of its container.

The following are the changes of state:

Changes of State

Solid → Liquid	Melting or fusion
Liquid → Gas	Vaporization
Liquid → Solid	Freezing
Gas → Liquid	Condensation
Solid → Gas	Sublimation

- If heat is added to a substance, such as in melting, vaporization, and sublimation, the process is **endothermic**, meaning that heat moves into the sample. In this instance, heat is increasing the speed of the molecules causing them move faster (examples: solid to liquid; liquid to gas; solid to gas).
- If heat is removed from a substance, such as in freezing and condensation, then the process is **exothermic**, meaning that heat moves out of the sample. In this instance, heat is decreasing the speed of the molecules causing them move slower (examples: liquid to solid; gas to liquid). These changes **release heat** to the surroundings.
- The amount of heat needed to change a sample from solid to liquid would be the same to reverse from liquid to solid. The only difference is the direction of heat transfer.

✓ Example 4.2.1

Label each of the following processes as endothermic or exothermic.

- a. water boiling
- b. hot gelatin solution cools in the refrigerator

Solution

- a. endothermic - you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
- b. exothermic - For another example, think of ice forming in your freezer. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

Exercise

Label each of the following processes as endothermic or exothermic.

- a. water vapor condensing
- b. gold melting

Answer

- a. exothermic
- b. endothermic

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H_2O) as an example. On the Celsius scale, H_2O has a melting point of 0°C and a boiling point of 100°C . At 0°C , both the solid and liquid phases of H_2O can coexist. However, if heat is added, some of the solid H_2O will melt and turn into liquid H_2O . If heat is removed, the opposite happens: some of the liquid H_2O turns into solid H_2O . A similar process can occur at 100°C : adding heat increases the amount of gaseous H_2O , while removing heat increases the amount of liquid H_2O (Figure 4.2.1).

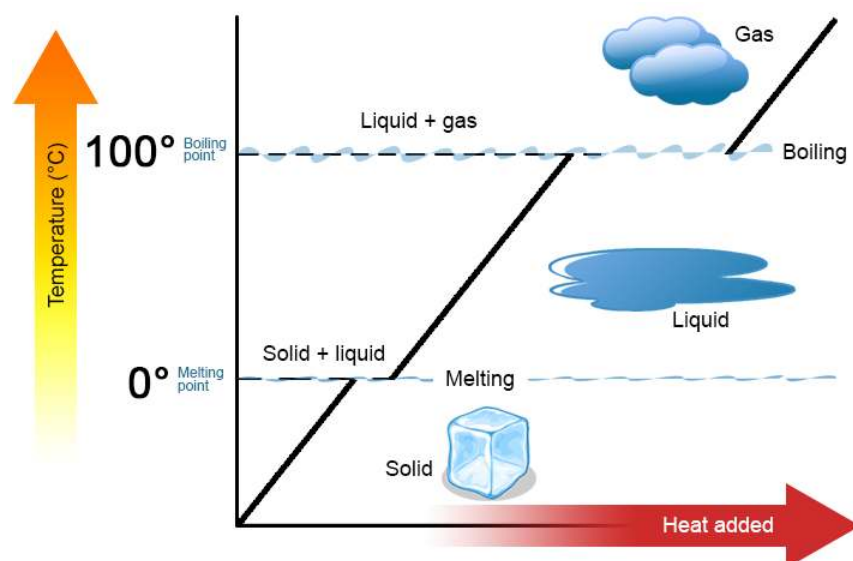
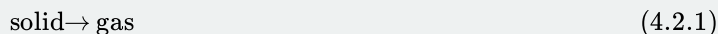


Figure 4.2.2: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (CC BY 3.0 Unported; Community College Consortium for Bioscience Credentials).

Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

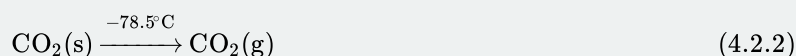
Sublimation and Quality of Frozen Foods

There is also a phase change where a solid goes directly to a gas:



This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At -78.5°C (-109°F), solid carbon dioxide sublimates, changing directly from the solid phase to the gas phase:



Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it goes directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C , solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimates, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimates, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a “burn,” and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer’s temperature and by wrapping foods tightly so water does not have any space to sublime into.

Key Takeaway

- There is an energy change associated with any phase change.

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4.3: 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, H₂O exists in the solid form as ice. When it is warmer, the liquid phase of H₂O is present. At even higher temperatures, H₂O 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 4.3.1 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 4.3.1: 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 ₂ O)	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**.

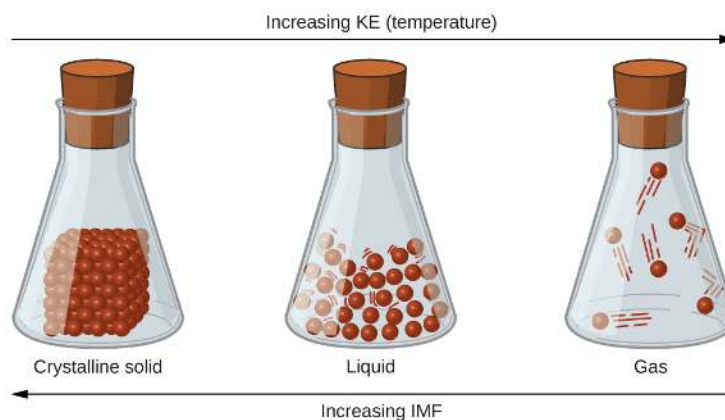


Figure 4.3.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

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 4.3.2). 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.

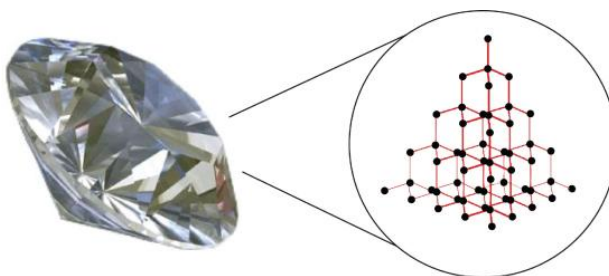


Figure 4.3.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

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 4.3.3) is an example of a substance whose particles experience ionic interactions (Table 4.3.1). These attractive forces are sometimes referred to as ion-ion interactions.

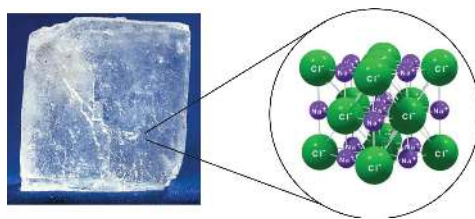


Figure 4.3.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

Covalent Molecular Compounds

There are two different covalent structures: molecular and network. Covalent network compounds like SiO₂ (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, 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**.

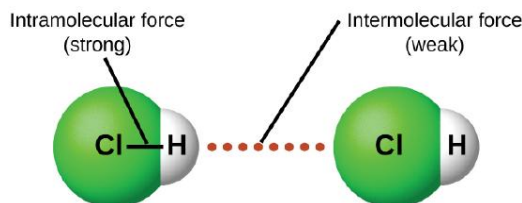


Figure 4.3.4: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties.

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 3.3.3, a 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 below).



Figure 4.3.5: 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 (CO₂) and carbon tetrachloride (CCl₄) are examples of such molecules (Figure 4.3.6).

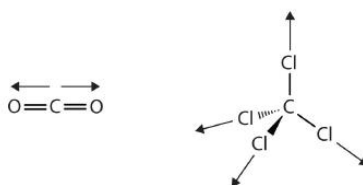


Figure 4.3.6: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

Recall from the Sections in Chapter 3, 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 4.3.7.

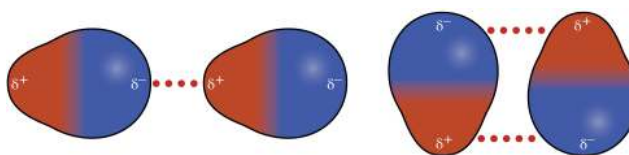


Figure 4.3.7: This image shows two arrangements of polar molecules, such as HCl , that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

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 4.3.1

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.

Exercise

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 $\text{HF} \cdots \text{HF}$, $\text{H}_2\text{O} \cdots \text{HOH}$, and $\text{H}_3\text{N} \cdots \text{HNH}_2$, in which the **hydrogen bonds** are denoted by **dots**. Figure 4.3.8 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.

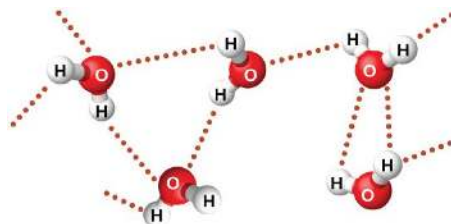


Figure 4.3.8: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

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 4.3.9 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:

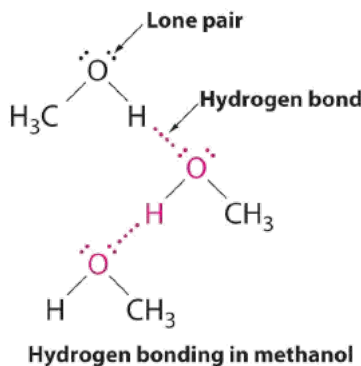


Figure 4.3.9: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

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 ($\text{CH}_3\text{CH}_2\text{OH}$), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). 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 , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CH}_3$ 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 $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, $\text{CH}_3\text{CH}_2\text{OH}$ has an $-\text{OH}$ 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 $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CH}_2\text{OH}$. 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 4.3.2

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 $-\text{NH}$ 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 .

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 the table below.

Table 4.3.2: 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

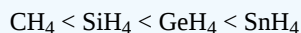
The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther 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 4.3.3

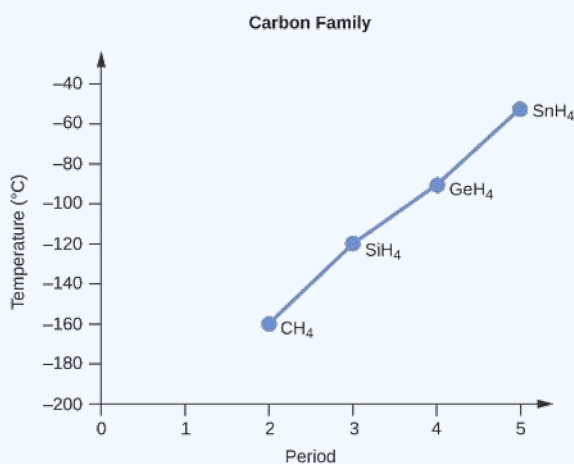
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4 , SiH_4 , GeH_4 , and SnH_4 . Explain your reasoning.

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



A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



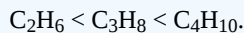
A line graph, titled "Carbon Family," is shown where the y-axis is labeled "Temperature, (degree sign C)" and has values of "negative 200" to "negative 40" from bottom to top in increments of 20. The x-axis is labeled "Period" and has values of "0" to "5" in increments of 1. The first point on the graph 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."

Exercise

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



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.

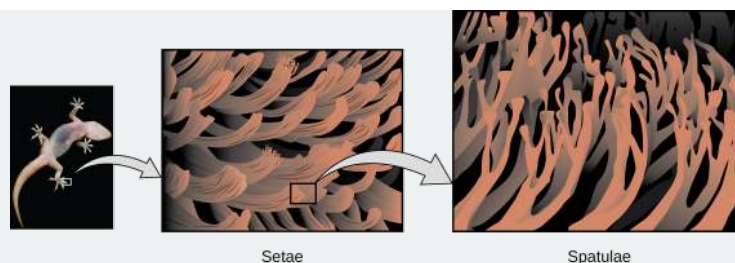


Figure 4.3.12: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos 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 the image above, 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 4.3.3: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point ($^{\circ}\text{C}$)
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 4.3.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

- potassium chloride (KCl)
- ethanol (C₂H₅OH)
- bromine (Br₂)

Solution

- 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.
- 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.)
- 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 4.3.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

- methylamine (CH₃NH₂)
- calcium sulfate (CaSO₄)
- carbon monoxide (CO)

Answer

- dipole-dipole, hydrogen bonding
- ionic forces (solid at room temperature)
- 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.

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CHAPTER OVERVIEW

5: Macronutrients - Carbohydrates

- 5.1: Carbohydrates
- 5.2: Classes of Monosaccharides and Handedness
- 5.3: Important Hexoses
- 5.4: Cyclic Structures of Monosaccharides
- 5.5: Sugars and Cooking
- 5.6: Disaccharides - Maltose, Lactose, and Sucrose
- 5.7: Polysaccharides - Starch, Glycogen, and Cellulose

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5.1: Carbohydrates

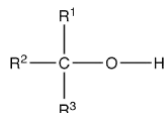
Learning Objectives

- To recognize carbohydrates as aldehydes or ketones containing many hydroxyl groups.

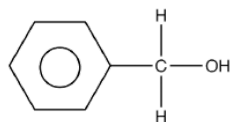
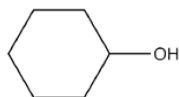
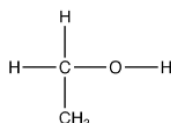
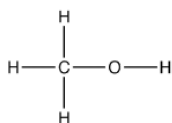
Three Important Organic Structures

Before we can begin our study of carbohydrates, you will need to become familiar with three organic structures: the **hydroxyl group** -OH, the **ketone**, and the **aldehyde**. These three structures become branches off the main carbon backbone of a carbohydrate molecule.

A hydroxyl group -OH in an organic compound creates an **alcohol** functional group that has the following general structure:

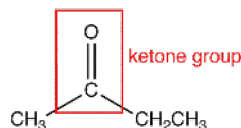


R1, R2, and R3 could be hydrogen atoms, other carbon atoms, rings of carbon atoms, or any combination thereof. For example:

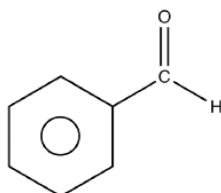
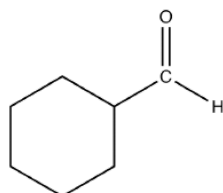
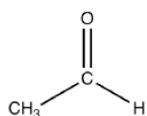
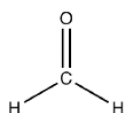


Two other important structures appear in carbohydrates. Both of these include a **carbonyl group**, identified by a carbon atom double-bonded to an oxygen atom: C=O. The term carbonyl is pronounced, "carbon-eel."

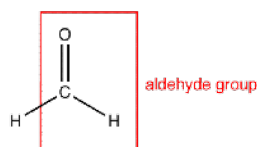
When the carbonyl group appears, it will qualify a compound to join a new class of molecules. When the carbonyl group is bonded to two other carbon atoms, the compound is called a **ketone**, and the carbonyl earns the name "the ketone group."



When the carbonyl group is bonded to a hydrogen atom, it creates a structure called an **aldehyde**. The other bond to the carbonyl group may be either a second hydrogen atom or a carbon atom. For example:

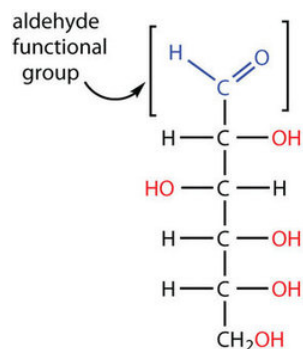


The CHO group in an aldehyde is called the aldehyde group.



Carbohydrates are aldehydes or ketones with extra hydroxyl groups

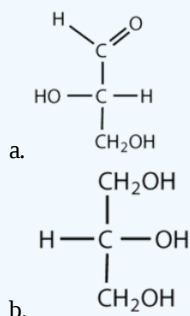
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $\text{C}_6\text{H}_{12}\text{O}_6$, glucose was once thought to be a “carbon hydrate” with the structure $\text{C}_6 \cdot 6\text{H}_2\text{O}$.

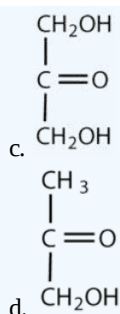


Because glucose has an aldehyde functional group and several $-\text{OH}$ (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

✓ Example 5.1.1

Which compounds would be classified as carbohydrates?



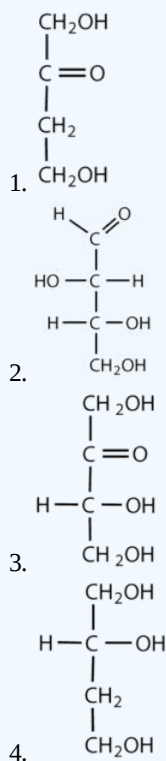


Solution

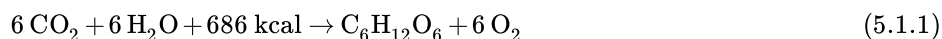
- This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
- This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
- This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
- 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 5.1.1

Which compounds would be classified as carbohydrates?



Green plants are capable of synthesizing glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:



(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material

of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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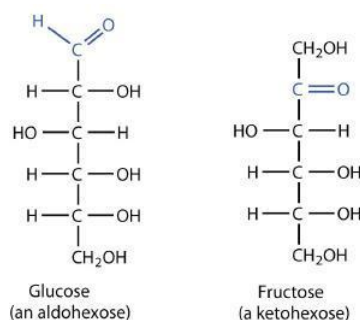
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5.2: Classes of Monosaccharides and Handedness

Learning Objectives

- Classify monosaccharides as aldoses or ketoses and as trioses, tetroses, pentoses, or hexoses.
- Observe and recognize the handedness of D- and L-saccharides.

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.



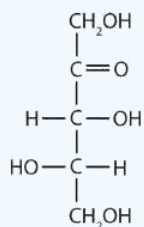
✓ Example 5.2.1

Draw an example of each type of compound.

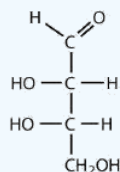
- a ketopentose
- an aldotetrose

Solution

- 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 5.2.1

Draw an example of each type of compound.

- an aldohexose
- a ketotetrose

The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure 5.2.1; 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 5.2.1. Molecules that are nonsuperimposable (nonidentical) mirror images of each other are a type of stereoisomer called **enantiomers** (Greek *enantios*, meaning “opposite”). We can think of pairs of molecules that are mirror images of each other much the same way we can consider right and left hands, which are mirror images of each other. This will be discussed more fully below.

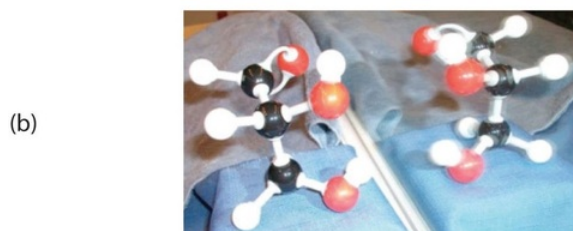
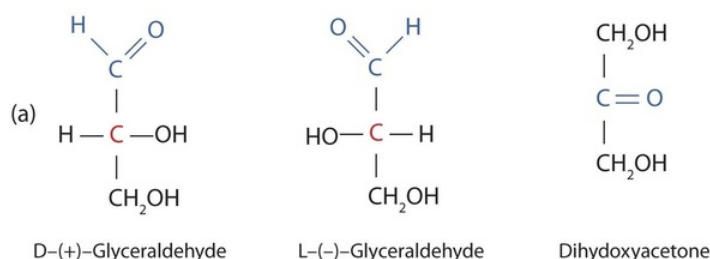


Figure 5.2.1: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

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 5.2.1). 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 $+8.7^\circ$, 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 5.2.1. 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.

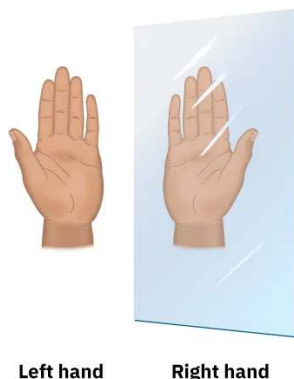
More on Mirror Images and Handedness in Molecules

Understanding the causes and consequences of molecular handedness is crucial to understanding organic and biomolecules.



Figure 5.1: Like the mountain whose image is reflected in a lake, many organic molecules also have mirror-image counterparts. (credit: modification of work “Crystal Lake sunrise reflection” by Sandy Horvath-Dori/Wikimedia Commons, CC BY 2.0)

Are you right-handed or left-handed? You may not spend much time thinking about it, but handedness plays a surprisingly large role in your daily activities. Many musical instruments, such as oboes and clarinets, have a handedness to them; the last available softball glove always fits the wrong hand. The reason for these difficulties is that our hands aren't identical; rather, they're *mirror images*. When you hold a left hand up to a mirror, the image you see looks like a right hand. Try it.



Handedness is also important in organic and biological chemistry, where it arises primarily as a consequence of carbon atoms that can bond to four different groups in a different mirror-image order. Many drugs and almost all the molecules in our bodies—amino acids, carbohydrates, nucleic acids, and many more—have a handedness. Furthermore, molecular handedness enables the precise interactions between enzymes and their substrates that are involved in the hundreds of thousands of chemical reactions on which life is based.

Summary

Monosaccharides can be classified by the number of carbon atoms in the structure and/or the type of carbonyl group they contain (aldose or ketose). Most monosaccharides contain at least one chiral carbon and can form stereoisomers. Enantiomers are a specific type of stereoisomers that are mirror images of each other.

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5.3: Important Hexoses

Learning Objectives

- To consider the structures of D-glucose, D-galactose, and D-fructose and identify their differences.
- Discuss the sweetness of the hexoses and compare them to common dietary sugar substitutes.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 5.3.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

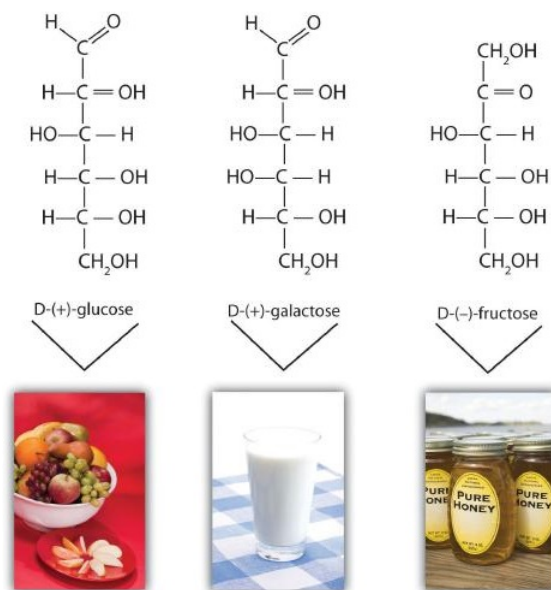


Figure 5.3.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

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.

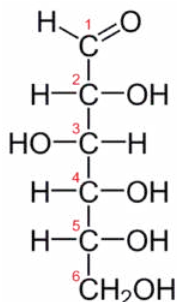


Figure 5.3.2: Fischer projection of D-glucose

The **Fischer projection** of D-glucose is given in Figure 5.3.2. 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 5.3.1. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure 5.3.1, 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 5.3.1).

Table 5.3.1: The Relative Sweetness of Some Compounds (Sucrose = 100)

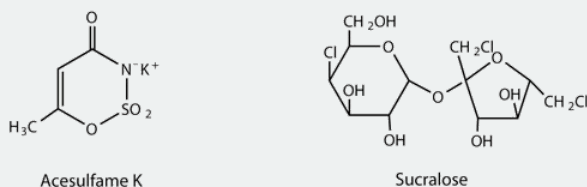
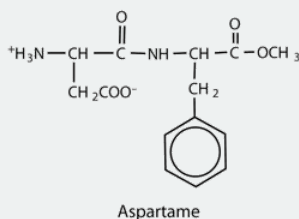
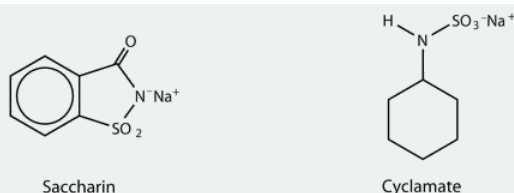
Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

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 U.S. 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.



A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease [phenylketonuria](#) (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is [sucralose](#), a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

Summary

Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.

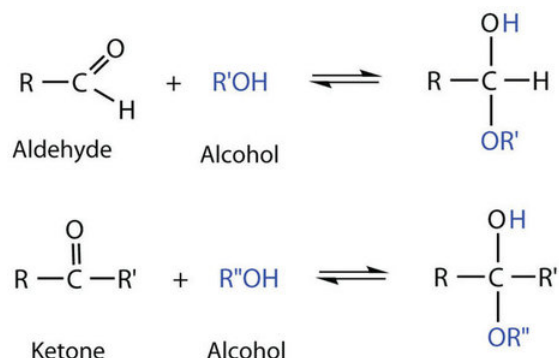
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5.4: Cyclic Structures of Monosaccharides

Learning Objectives

- Be able to identify a cyclic monosaccharide from its structure.

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.

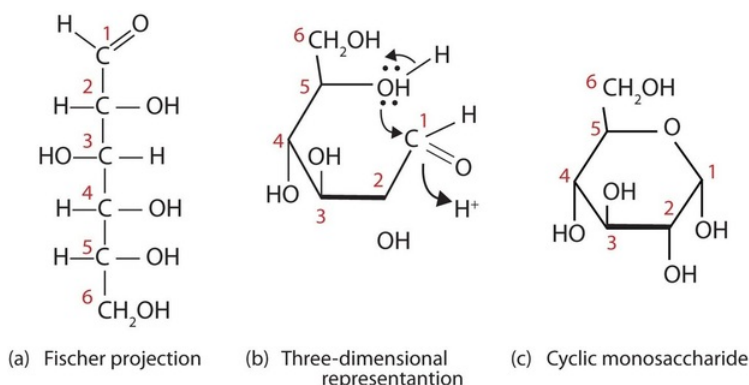


Figure 5.4.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide, such as any of the structures shown in Figure 5.4.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 5.4.2. The structure shown on the left side of Figure 5.4.2, 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 , while the β form melts at 150°C . 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 5.4.2). 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.

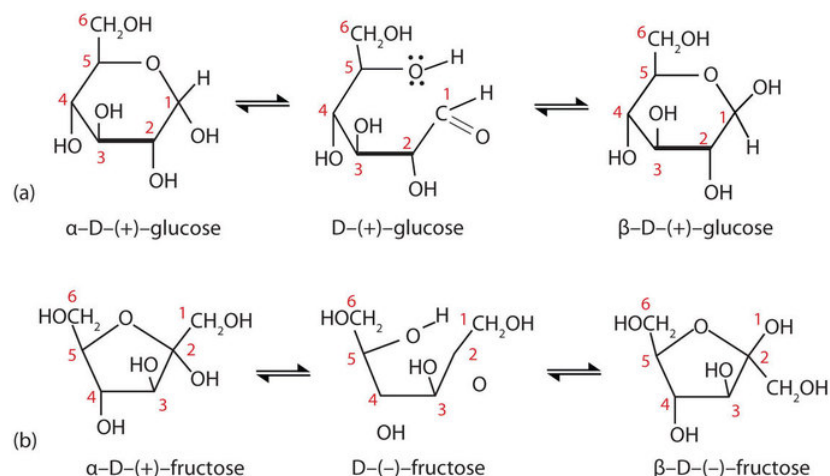


Figure 5.4.2: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Commonly, (e.g., in Figures 5.4.1 and 5.4.2) 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 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.

Can you identify monosaccharides at a glance?

Monosaccharides can be represented as either the Fischer projection (straight line) form or in the cyclic form, usually drawn with a Haworth projection. From the examples given in this section and the previous section, you should be able to identify a monosaccharide at a glance. You are not responsible for naming the compounds, identifying the anomeric carbons, whether they are D- or L-saccharides, or whether they are α or β . But you should be able to state whether you see a saccharide in front of you.

Summary

Monosaccharides that contain five or more carbon atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. In an aqueous solution, an equilibrium mixture forms between the two anomers and the straight-chain structure of a monosaccharide in a process known as mutarotation.

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5.5: Sugars and Cooking

Learning Objectives

- To recognize that there are other classes of saccharides
- To consider the role of the role of the disaccharide sucrose - household sugar - in cooking

Monosaccharides are common in foods. For example, glucose is commonly known as "grape sugar" and is found abundantly in honey. Fructose is found in fruits and therefore is often called "fruit sugar." Pure monosaccharides 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.

However, there are many other types of saccharides. Consider, for example, household sugar, which is a disaccharide called sucrose. Before we look ahead to the structure of sucrose and other disaccharides, pause for some context about why sugars - both disaccharides and monosaccharides, and their cousins the polysaccharides - are so important to the science of cooking.

Sugar - sucrose - is the third most used ingredient in the bakeshop. Sugar has several functions in baking. The most recognized purpose is, of course, to sweeten food, but there are many other reasons sugar is used in cooking and baking:

- It can be used for browning effect, both caramelization and the Maillard reaction, on everything from breads to cookies to cakes. Browning gives a pleasant colour and flavour to the finished product. Caramelization results from the action of heat on sugars. At high temperatures, the chemical changes associated with melting sugars result in a deep brown colour and new flavours. The Maillard reaction results from chemical interactions between sugars and proteins at high heat. An amino group from a protein combines with a reducing sugar to produce a brown colour in a variety of foods (e.g., brewed coffee, fried foods, and breads).
- It acts as the most important tenderizing agent in all baked goods, and one of the factors responsible for the spread in cookies. It helps delay the formation of gluten, which is essential for maintaining a soft or tender product.
- It makes an important contribution to the way we perceive the texture of food. For example, adding sugar to ice cream provides body and texture, which is perceived as smoothness. This addition helps prevent lactose crystallization and thus reduces sugar crystal formation that otherwise causes a grainy texture sometimes associated with frozen dairy products.
- It preserves food when used in sufficient quantity.
- In baking, it increases the effectiveness of yeast by providing an immediate and more usable source of nourishment for the yeast's growth. This hastens the leavening process by producing more carbon dioxide, which allows the dough to rise at a quicker and more consistent rate.

Just as there are many functions of sugar in the bakeshop, there are different uses for the various types of sugar as well:

- Fine granulated sugar is most used by bakers. It generally dissolves easily in mixes and is pure enough for sugar crafters to boil for "pulled" sugar decorations.
- Coarse granulated sugar may be used for a topping on sugar cookies, puff pastry, and Danish pastries as it doesn't liquefy or caramelize so readily. In some European countries, an extra coarse sugar (called hail — a literal translation) is used for this purpose.
- Icing or powdered sugar is used in icings and fillings and in sifted form as a top decoration on many baked goods.
- Brown or yellow sugars are used where their unique flavor is important, or in bakeries where an old-fashioned or rustic image is projected. Brown sugar can usually be substituted for white sugar without technical problems in sugar/batter mixes such as cakes and muffins, and in bread dough.

Summary

Monosaccharides include glucose and fructose. Yet there are many other classes of sugars, including the disaccharide sucrose and polysaccharides. Sugars are used for many purposes in cooking.

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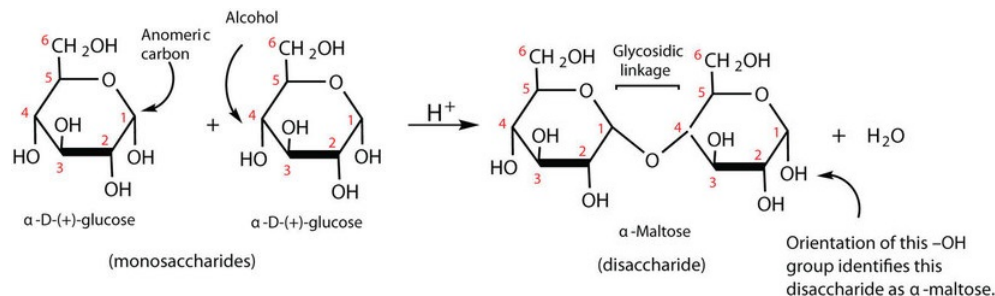
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5.6: Disaccharides - Maltose, Lactose, and Sucrose

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.

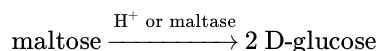


The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll 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.



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 5.6.1. This creates two different isomers of maltose.

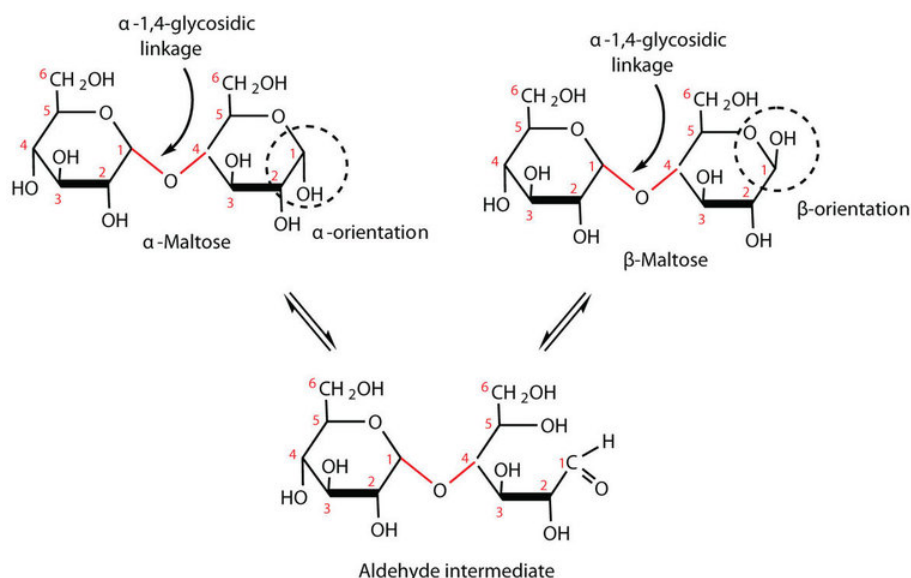
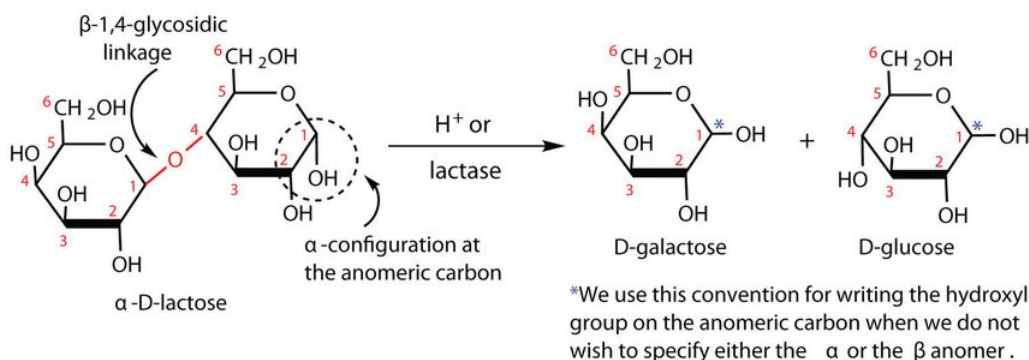


Figure 5.6.1: An Equilibrium Mixture of Maltose Isomers

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.

✓ 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.

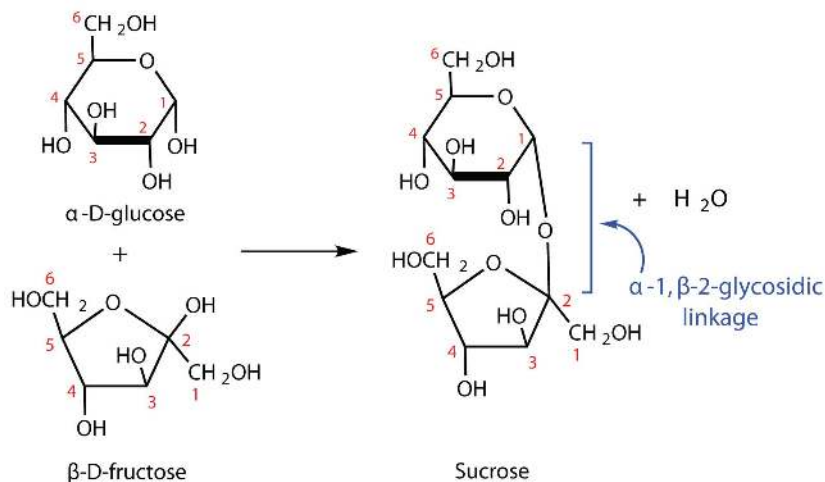
In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water 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 linkage between fructose and glucose 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 exists in only one form both in the solid state and in solution.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as *invertase*) gives mixture that will be half glucose and half fructose. This 1:1 mixture is referred to as *invert sugar* or *simple syrup* which can be purchased for use in cooking. It is about 30% sweeter than table sugar. While sucrose readily recrystallizes from a solution, invert sugar has a much greater tendency to remain dissolved. 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, pre-sweetened 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.

Can you identify disaccharides at a glance?

Disaccharides are usually drawn with a Haworth projection using the cyclic forms you see in the examples above. From the examples given in this section and the previous section, you should be able to identify a disaccharide at a glance compared to a monosaccharide. You are not responsible for naming the compounds, identifying the anomeric carbons, whether they are D- or L-saccharides, or whether they are α or β . But you should be able state whether you see a disaccharide in front of you.

Summary

Maltose is composed of two molecules of glucose and is found in sprouting grain. Lactose is composed of a molecule of galactose joined to a molecule of glucose and is a sugar that is found in milk. Sucrose is composed of a molecule of glucose joined to a molecule of fructose and is found in sugar cane and sugar beets.

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5.7: Polysaccharides - Starch, Glycogen, and Cellulose

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 5.7.1). 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 5.7.1). 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.

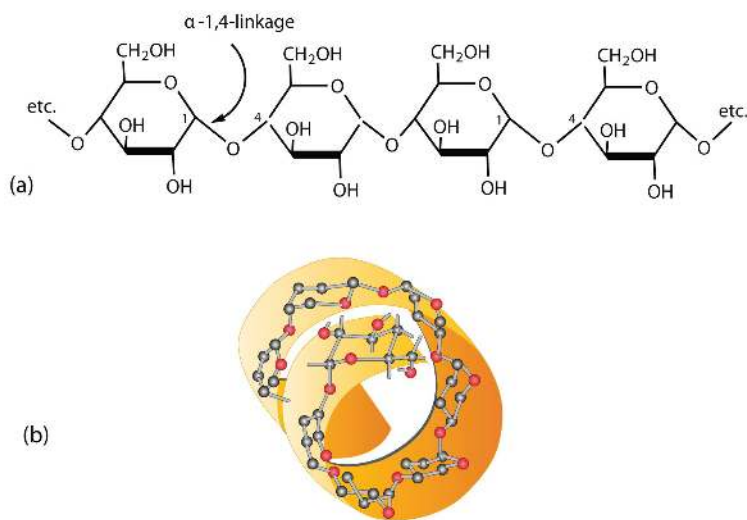


Figure 5.7.1: Amylose. (a) Amylose is a linear chain of α -D-glucose units joined together by α -1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

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 5.7.2). 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.

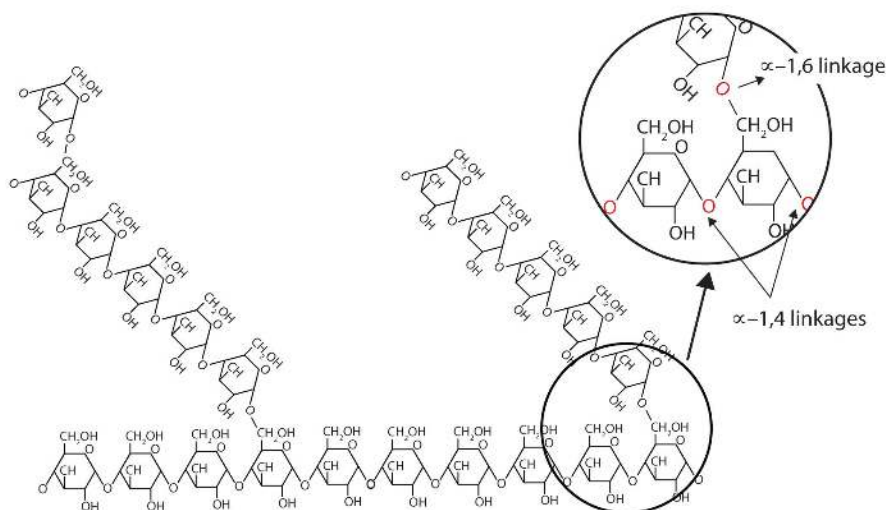
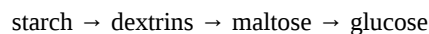


Figure 5.7.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α -1,6-linkages. These branch points occur more often in glycogen.

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:



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 5.7.3). 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 5.7.3). 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.

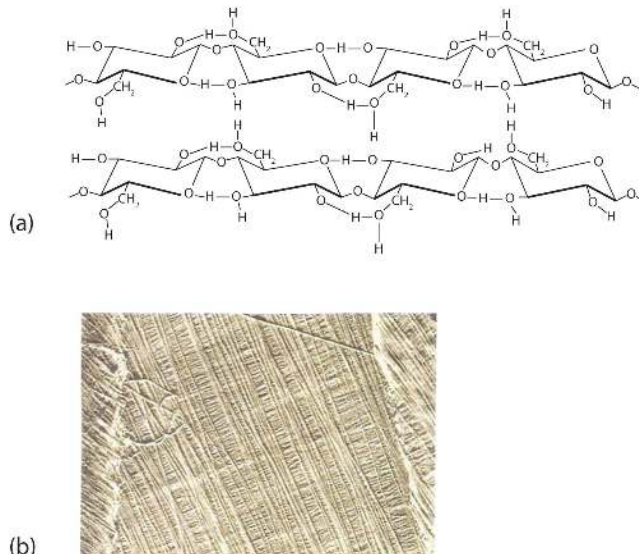


Figure 5.7.3: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β -glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Summary

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin. Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β -1,4-glycosidic bonds.

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CHAPTER OVERVIEW

6: Macronutrients - Fats

6.1: Fatty Acids

6.2: Fats and Oils

6.3: Membranes and Membrane Lipids

6.4: Steroids

6.5: Lipids (Summary)

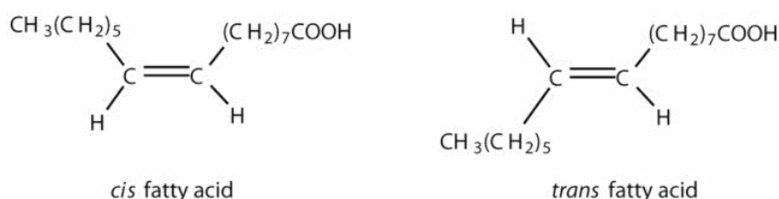
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6.1: Fatty Acids

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table 6.1.1 lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table 6.1.1: Some Common Fatty Acids Found in Natural Fats

Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$\text{C}_{11}\text{H}_{23}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	44	palm kernel oil
myristic acid	$\text{C}_{13}\text{H}_{27}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	58	oil of nutmeg
palmitic acid	$\text{C}_{15}\text{H}_{31}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	63	palm oil
palmitoleic acid	$\text{C}_{15}\text{H}_{29}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	0.5	macadamia oil
stearic acid	$\text{C}_{17}\text{H}_{35}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	70	cocoa butter
oleic acid	$\text{C}_{17}\text{H}_{33}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	16	olive oil
linoleic acid	$\text{C}_{17}\text{H}_{31}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{CH}=\text{CH})_2(\text{CH}_2)_7\text{COOH}$	−5	canola oil
α-linolenic acid	$\text{C}_{17}\text{H}_{29}\text{COOH}$	$\text{CH}_3(\text{CH}_2\text{CH}=\text{CH})_3(\text{CH}_2)_7\text{COOH}$	−11	flaxseed
arachidonic acid	$\text{C}_{19}\text{H}_{31}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_4(\text{CH}_2\text{CH}=\text{CH})_4(\text{CH}_2)_2\text{COOH}$	−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.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure 6.1.2*a*). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure 6.1.2*b*). Such molecules pack closely together into a crystal lattice, maximizing the strength of dispersion forces and causing fatty acids and the fats derived from them to have relatively high melting points. In contrast, each *cis* carbon-to-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the intermolecular attractions of unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most are liquids at room temperature.

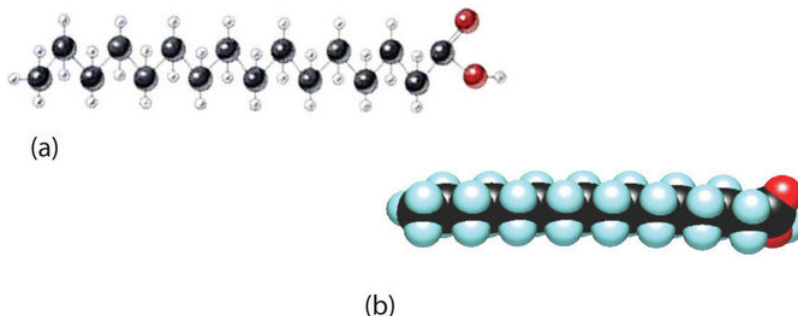
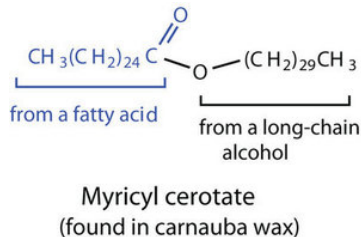


Figure 6.1.2: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

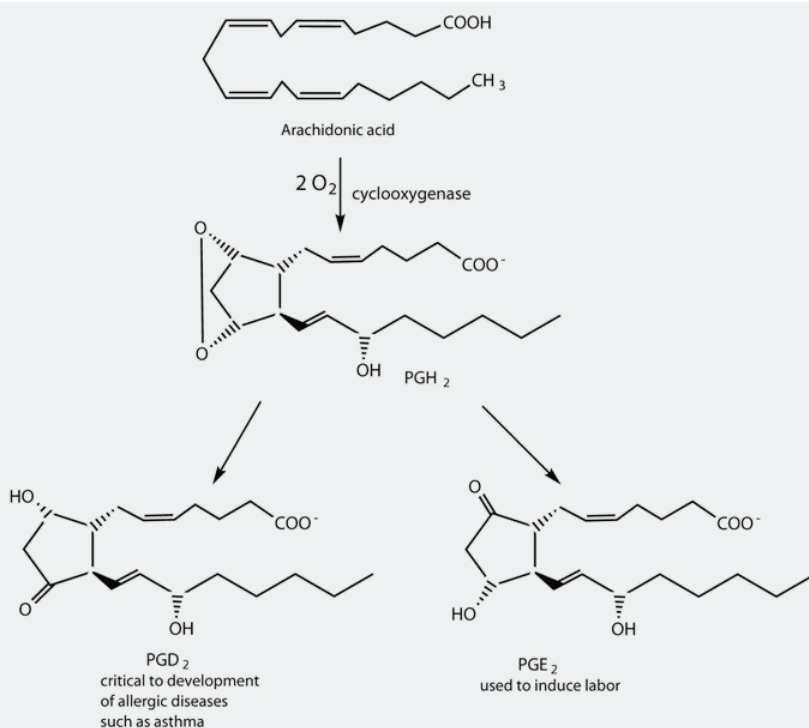
Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Optional Topic. 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 PGE₂ 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.

✓ Example 6.1.1

Give an example of each compound, using the table above for reference.

- saturated fatty acid
- polyunsaturated fatty acid
- monounsaturated fatty acid

Answer a

For example, **stearic acid** contains only single bonds between all of the carbon atoms.

Answer b

For example, **linoleic acid** contains several C=C double bonds.

Answer c

For example, **palmitoleic acid** contains one C=C double bond.

? Exercise 6.1.1

Classify each fatty acid as saturated or unsaturated.

- myristic acid
- oleic acid
- lauric acid

Answer a

Saturated

Answer b

Unsaturated, in fact oleic acid is monounsaturated

Answer c

Saturated

Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

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6.2: Fats and Oils

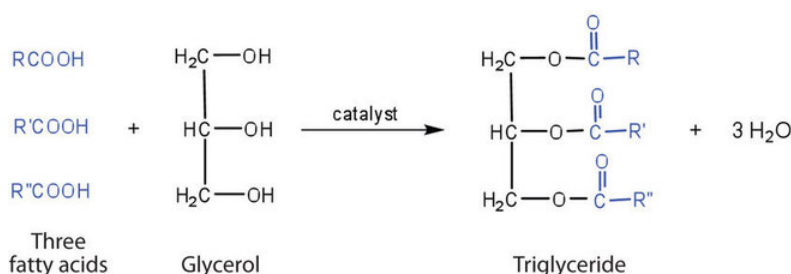
Learning Objectives

- 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 saponification (hydrolysis), hydrogenation, and oxidation.

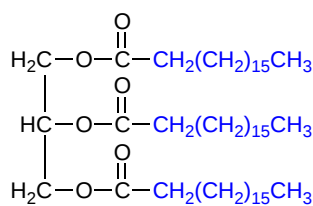
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

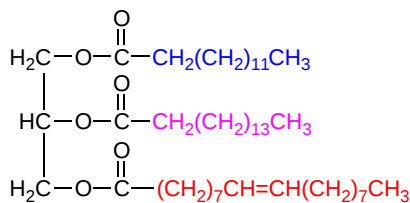
Fats and oils are called triglycerides (or *triacylglycerols*) because they are composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are joined 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 6.2.1 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.

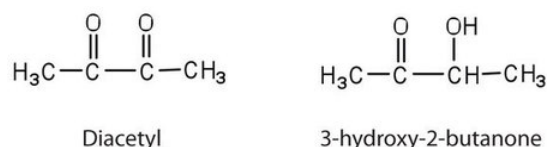
Table 6.2.1: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

	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

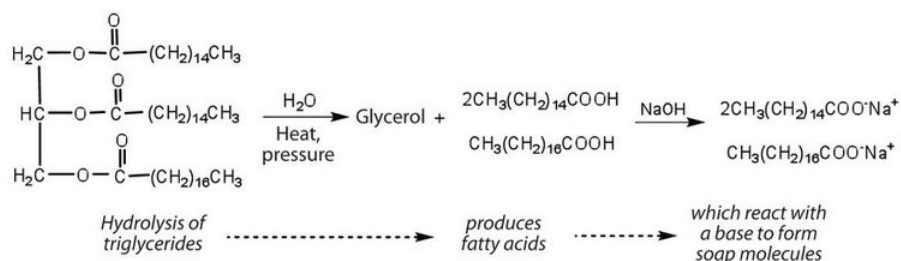
Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are soluble in the fats and oils. For example, the yellow color of butter is due to 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.



Fats and oils are lighter than water, having densities of about 0.8 g/mL. (Water has a density of 1.0 g/mL.) 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.

Saponification: Separating Fatty Acids from Glycerol

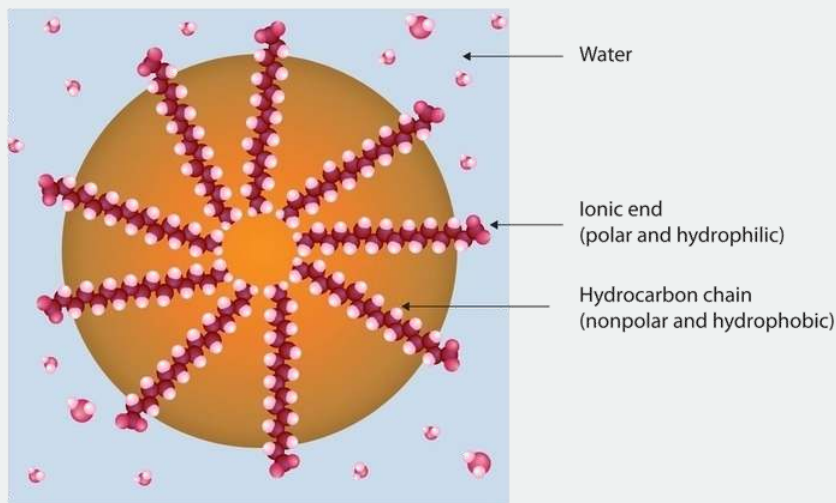
Fats and oils can participate in a variety of chemical reactions—for example, triglycerides they can be separated into glycerol and fatty acids in the presence of an acid, a base, or specific enzymes known as lipases. This so-called **hydrolysis** of fats and oils in the presence of a base is used to 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. 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.

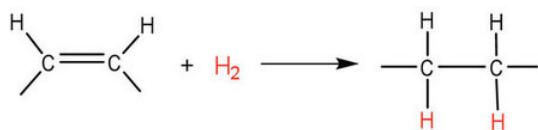
Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. 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.

Hydrogenation

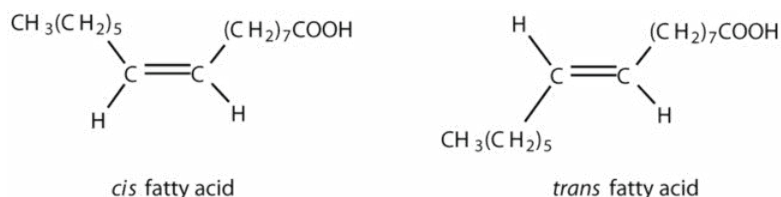
The double bonds in fats and oils can undergo **hydrogenation** and also **oxidation**. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry.



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 nutritional profile 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 prefer a spreadable oil to a pourable oil on breads.

Trans Fats in Foods

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 Section 6.1. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease, and are considered more dangerous to heart health than the saturated fats they were meant to replace. There is a structural reason for this: *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.

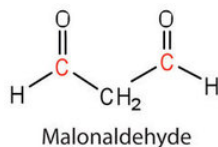
Rancidity in Fats and Oils

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 shorter-chain fatty acids. Rancid butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit



in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.



Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the

supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

Summary

Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

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6.3: 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 6.3.1A) and animal cells (Figure 6.3.1B) 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.

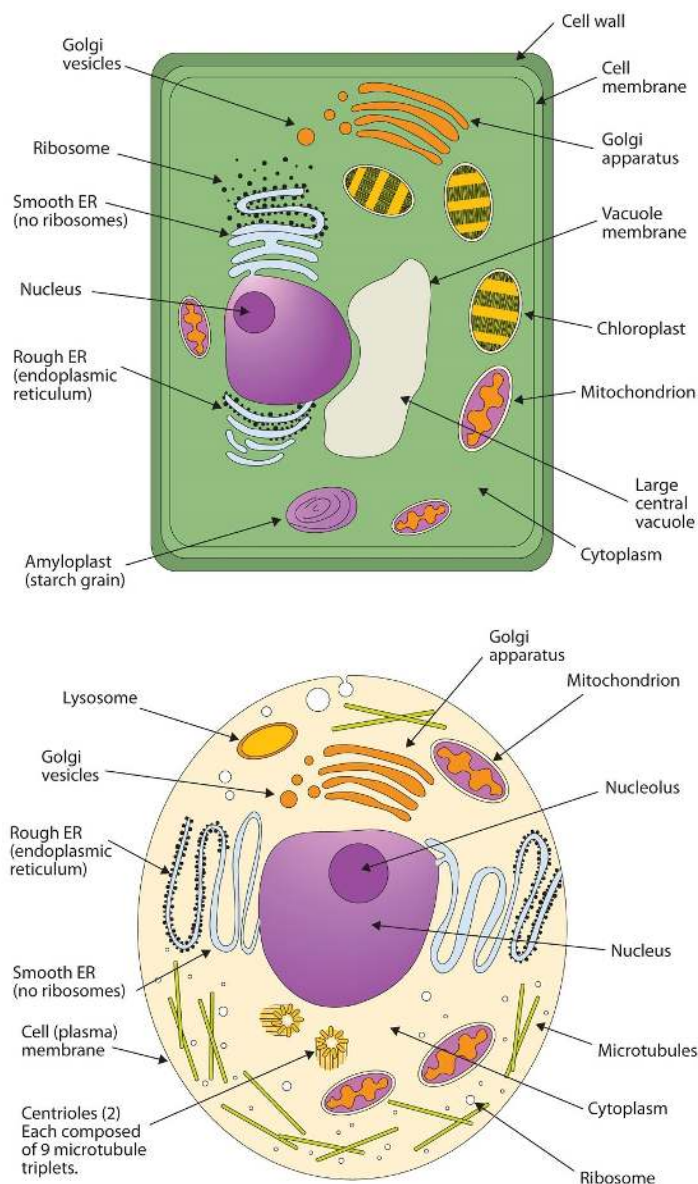


Figure 6.3.1: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

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 6.3.2).

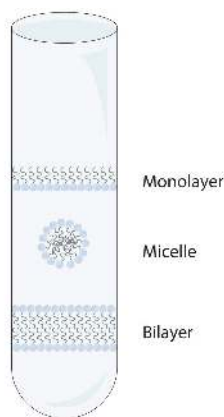


Figure 6.3.2: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

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 6.3.3).

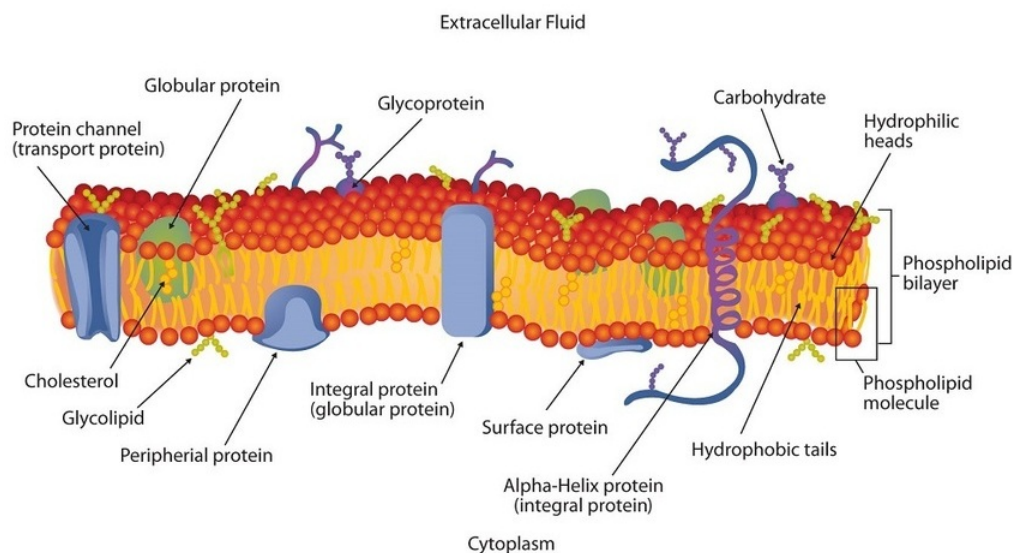


Figure 6.3.3: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

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 6.3.4.

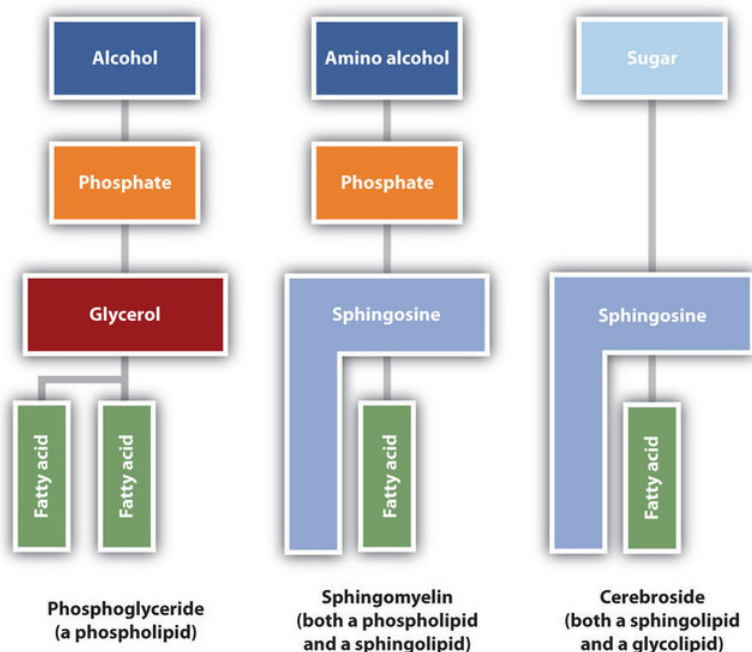


Figure 6.3.4: Component Structures of Some Important Membrane Lipids

Phosphoglycerides are composed of alcohol, phosphate, glycerol and 2 fatty acids. A sphingomyelin contains phosphate, sphingosine, and a fatty acid. A cerebroside 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 6.3.5) is attached to the third carbon atom of glycerol (part (b) of Figure 6.3.5). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure 6.3.5).

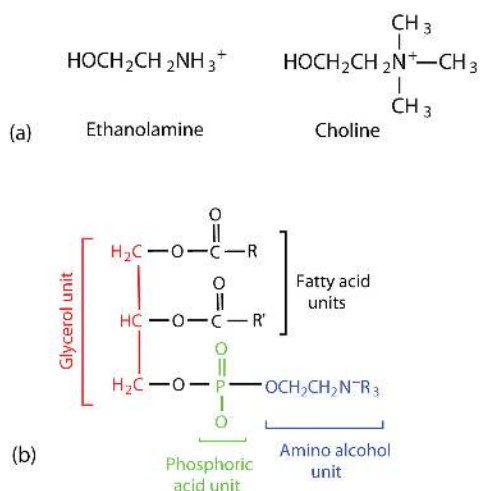
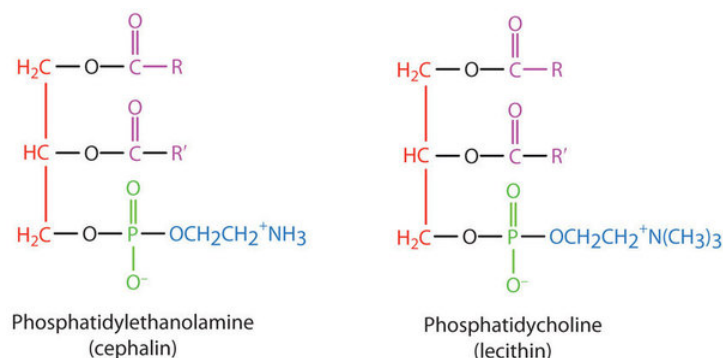


Figure 6.3.5: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

Structural formula of ethanolamine and choline are shown. The structural formula of a phosphoglyceride is shown with the glycerol unit, phosphoric unit, and amino alcohol unit highlighted in different colors.

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all

living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.



Sphingomyelins, the simplest sphingolipids, each contain a fatty acid, a phosphoric acid, sphingosine, and choline (Figure 6.3.6). Because they contain phosphoric acid, they are also classified as phospholipids. Sphingomyelins are important constituents of the myelin sheath surrounding the axon of a nerve cell. Multiple sclerosis is one of several diseases resulting from damage to the myelin sheath.

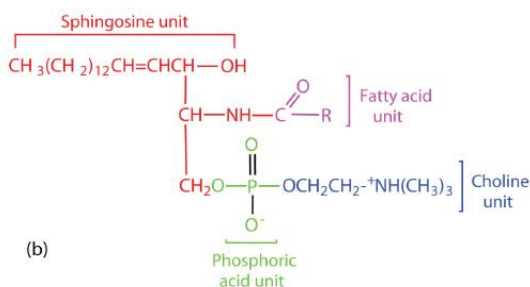
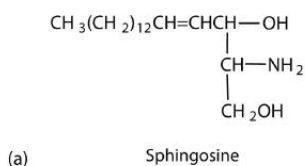


Figure 6.3.6: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

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 cerebroside (Figure 6.3.7). Cerebroside is 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. Cerebroside is an important constituent of the membranes of nerve and brain cells.

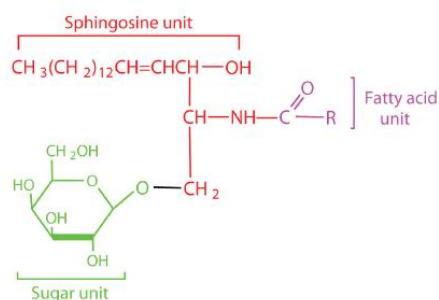


Figure 6.3.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.

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 6.3.3). 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.

Can you identify fatty acids and their related lipids at a glance?

From the images presented in this chapter so far, you should be getting familiar with the appearance of fatty acids - their nonpolar hydrocarbon tails and their polar heads. It is through the polar heads that we see bonds to other molecules - glycerol, sugars, phosphate groups, and more. But the general presence of the fatty acids tails is a hallmark of this class of compounds and the biomolecules that are formed from fatty acids. You should be able to identify fatty acids - saturated and unsaturated - and their related biomolecules at a glance. You are not required to name any of the compounds or classify the biomolecules formed from fatty acids.

Summary

Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

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6.4: Steroids

Learning Objectives

- Use the structure of the steroid skeleton to recognize the presence of a steroid
- Identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous base solution 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 base. The most important *nonsaponifiable* lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).

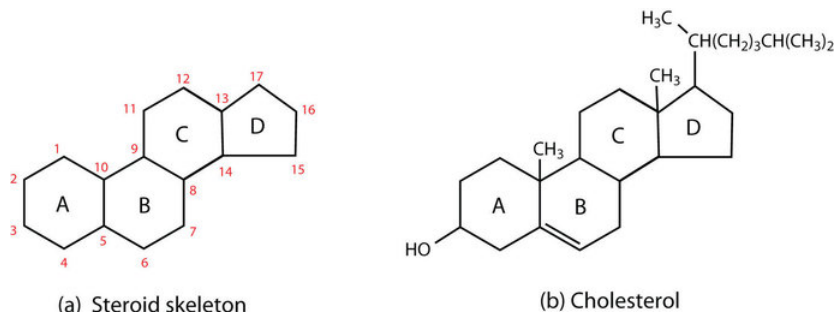


Figure 6.4.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

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 6.4.1a. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 6.4.1b) 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 6.4.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



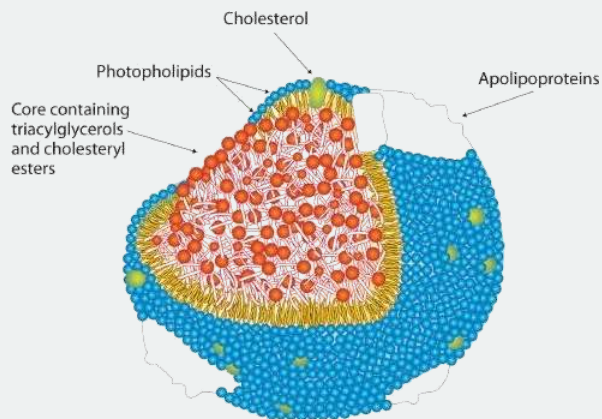
Figure 6.4.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

📌 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.

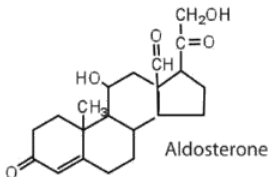
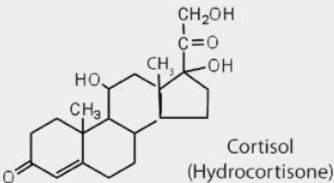
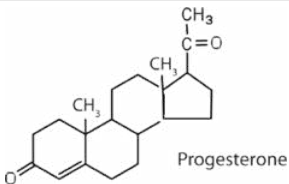
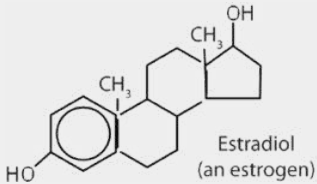
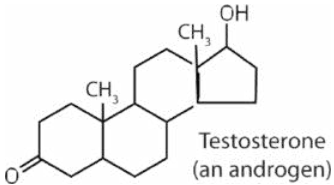
Steroid Hormones

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 6.4.1), 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 6.4.1: 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 6.4.3) and an amine such as the amino acid glycine (part (b) of Figure 6.4.3). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

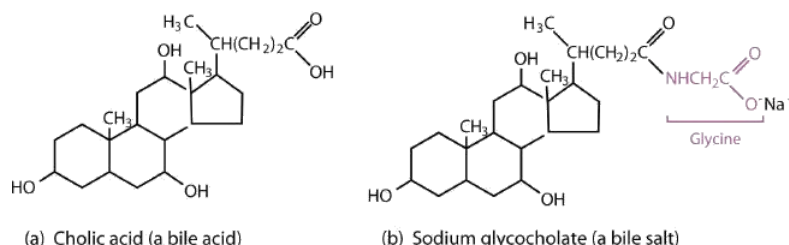


Figure 6.4.3 Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

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.

Can you identify steroids at a glance?

A helpful way to remember the basic structure of a steroid is to focus on the four rings in the structure. The presence of the rings indicate that you are looking at a compound that belongs to the steroid family. Some chemists nickname the ring structure "three rooms and a garage". You should be able to identify steroids at a glance, and recall they are a member of the lipid family of biomolecules. You are not required to name any of the compounds or classify the biomolecules formed from the basic steroid ring structure.

Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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6.5: Lipids (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Lipids, found in the body tissues of all organisms, are compounds that are more soluble in organic solvents than in water. Many of them contain **fatty acids**, which are carboxylic acids that generally contain an even number of 4–20 carbon atoms in an unbranched chain. **Saturated fatty acids** have no carbon-to-carbon double bonds. **Monounsaturated fatty acids** have a single carbon-to-carbon double bond, while **polyunsaturated fatty acids** have more than one carbon-to-carbon double bond. Linoleic and linolenic acid are known as **essential fatty acids** because the human body cannot synthesize these polyunsaturated fatty acids. The lipids known as **fats** and **oils** are triacylglycerols, more commonly called **triglycerides**—esters composed of three fatty acids joined to the trihydroxy alcohol glycerol. Fats are triglycerides that are solid at room temperature, and oils are triglycerides that are liquid at room temperature. Fats are found mainly in animals, and oils found mainly in plants. *Saturated triglycerides* are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglycerides* contain a higher proportion of unsaturated fatty acid chains.

Saponification is the hydrolysis of a triglyceride in a basic solution to form glycerol and three carboxylate anions or soap molecules. Other important reactions are the hydrogenation and oxidation of double bonds in unsaturated fats and oils.

Phospholipids are lipids containing phosphorus. In **phosphoglycerides**, the phosphorus is joined to an amino alcohol unit. Some phosphoglycerides, like lecithins, are used to stabilize an **emulsion**—a dispersion of two liquids that do not normally mix, such as oil and water. **Sphingolipids** are lipids for which the precursor is the amino alcohol sphingosine, rather than glycerol. A **glycolipid** has a sugar substituted at one of the OH groups of either glycerol or sphingosine. All are highly polar lipids found in cell membranes.

Polar lipids have dual characteristics: one part of the molecule is ionic and dissolves in water; the rest has a hydrocarbon structure and dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic** (literally, “water loving”) and the nonpolar part as **hydrophobic** (“water fearing”). When placed in water, polar lipids disperse into any one of three arrangements: *micelles*, *monolayers*, and *bilayers*. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

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CHAPTER OVERVIEW

7: Macronutrients - Proteins

[7.1: Properties of Amino Acids](#)

[7.2: Peptides](#)

[7.3: Proteins](#)

[7.4: Enzymes](#)

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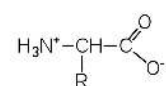
7.1: Properties of Amino Acids

Learning Objectives

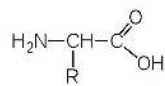
- To recognize amino acids and classify them based on the characteristics of their side chains.

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



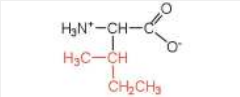
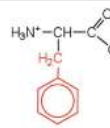
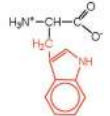
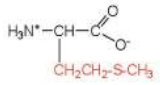
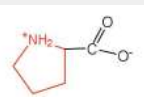
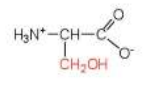
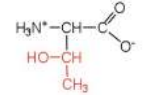
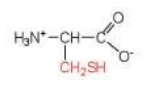
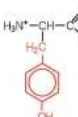
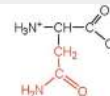
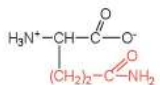
α -Amino acid drawn as an uncharged molecule; not an accurate representation of amino acid structure

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 7.1.1.

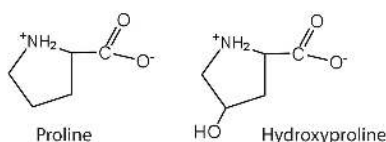
Table 7.1.1: Common Amino Acids Found in Proteins

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 <i>cystine</i>
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				

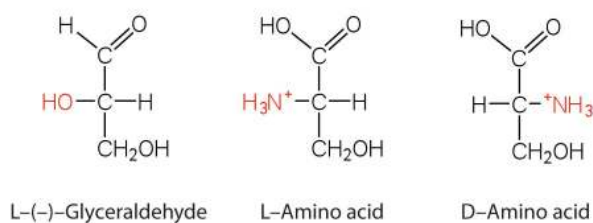
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pKa (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Configuration

Notice in Table 7.1.1 that glycine is the only amino acid whose α -carbon does not exhibit handedness - that is, is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-mirror images.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

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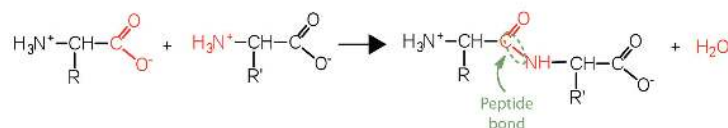
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7.2: Peptides

Learning Objectives

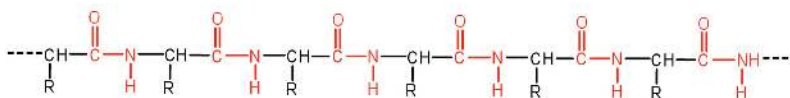
- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

Two or more amino acids can join together into chains called peptides. Consider below the reaction between the amino group on one amino acid molecule reacting with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:

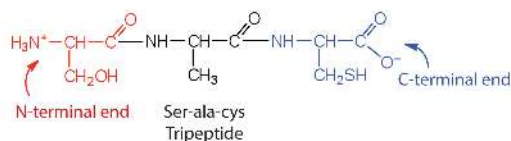


An amide bond joining two amino acid units is called a **peptide bond**. The reaction to form the peptide bond is often called a condensation reaction because the two starting amino acids "condense" to form a new molecule.

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. Note that the "R" notation stands in for the side chain of any possible amino acid.



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.

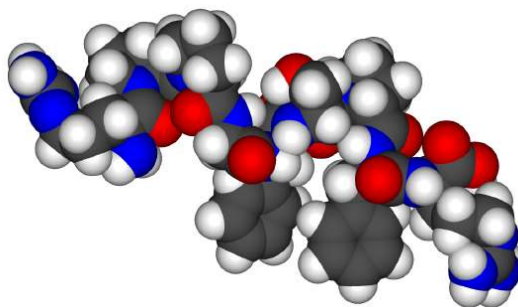


Figure 7.2.1: Space-filling model of the peptide bradykinin. (Public Domain; Fvasconcellos)

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 7.2.1) 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 is usually fatal.

Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

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7.3: 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 7.3.1.

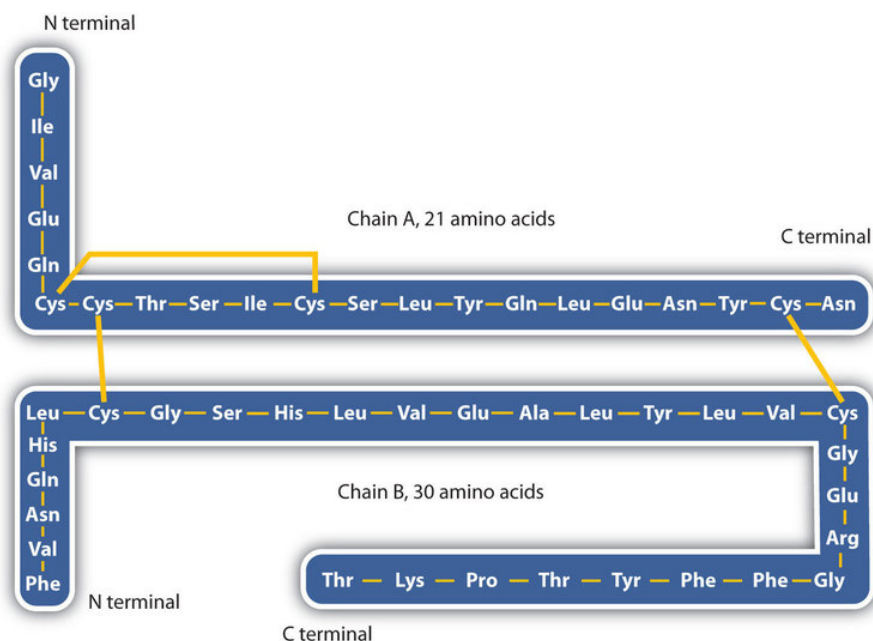


Figure 7.3.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

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 7.3.2). 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.

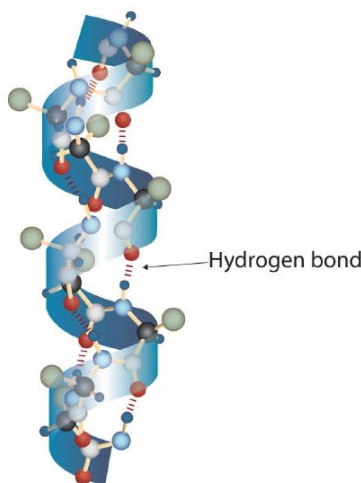


Figure 7.3.2 A Ball-and-Stick Model of an α -Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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 7.3.3). 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.

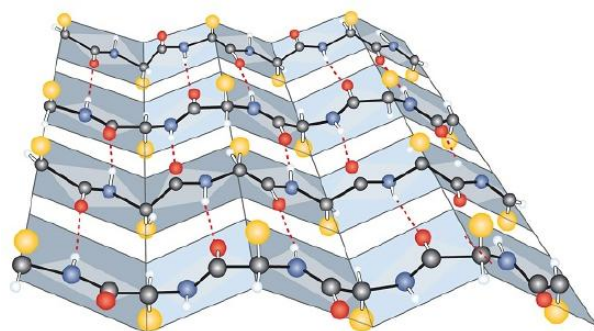


Figure 7.3.3: A Ball-and-Stick Model of the β -Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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 7.3.4 shows a depiction of the three-dimensional structure of insulin.

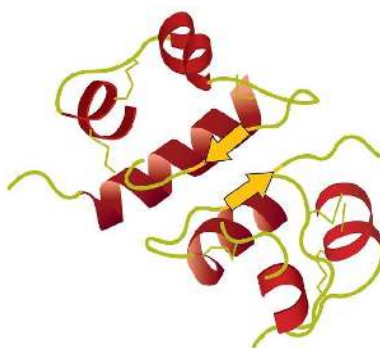
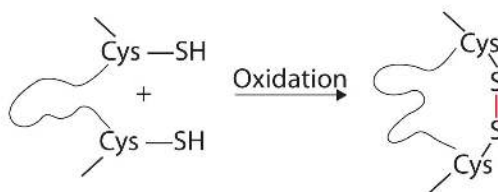


Figure 7.3.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α -helical structure, while the broad arrows represent β -pleated sheet structures.

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 7.3.5).
2. **Hydrogen bonding.** Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 7.3.5).
3. **Disulfide linkages.** Two cysteine amino acid units, with their -S-H features, may be brought close together as the protein molecule folds. Two nearby -SH groups can react to form a -S-S- bridge that can link different parts of a peptide chain to each other (part (c) of Figure 7.3.5). These intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 7.3.1) and have a strong stabilizing effect on the tertiary structure.



4. **Dispersion forces.** Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of

Figure 7.3.5). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

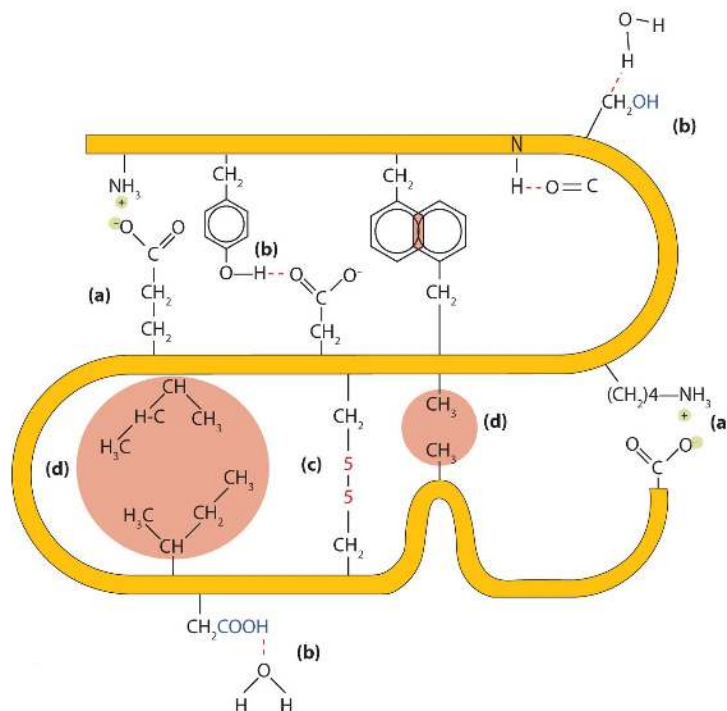


Figure 7.3.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 7.3.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 7.3.7.



Figure 7.3.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body. Each subunit in this image represents one of the four subunits: green, blue, red, and yellow.

Source: Image from the RCSB PDB ([www.pdb.org\(opens in new window\)](http://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).

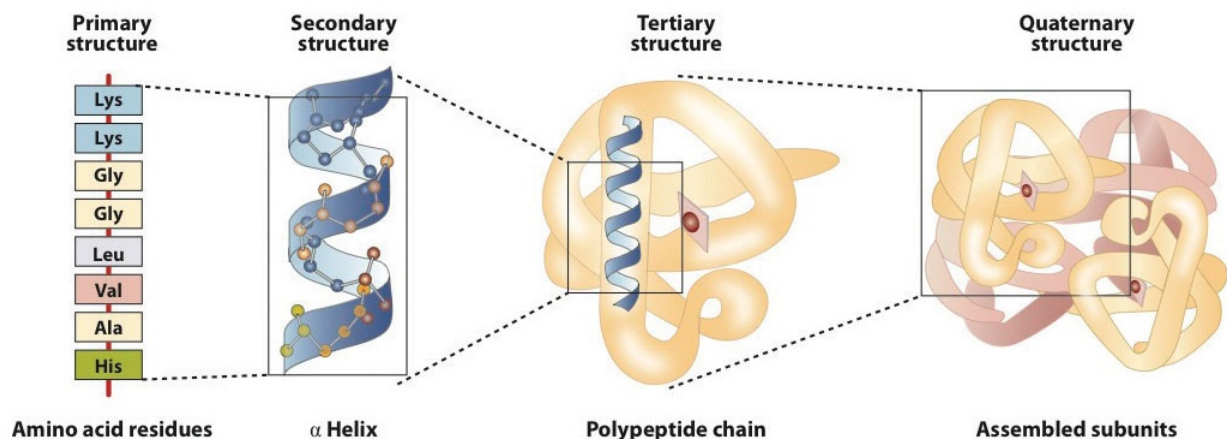


Figure 7.3.7: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α -helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 7.3.1).

Figure 7.3.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.
Large changes in pH	Addition (or subtraction) of H^+ ions can change the charges on amino acids with acidic and basic side-chains.

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 7.3.8). Such evidence

suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

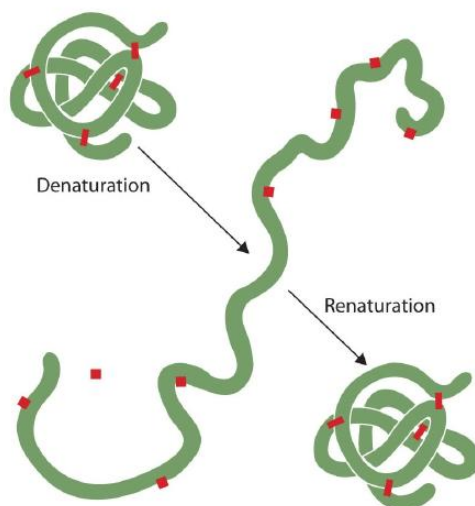


Figure 7.3.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α -helix or β -pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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7.4: Enzymes

Learning Objectives

- Explain the functions of enzymes.
- Explain how enzymes are classified and named.

A catalyst is any substance that increases the *rate* or speed of a chemical reaction without being changed or consumed in the reaction. Enzymes are biological catalysts, and nearly all of them are proteins. The reaction rates attained by enzymes are truly amazing. In their presence, reactions occur at rates that are a million (10^6) or more times faster than would be attainable in their absence. What is even more amazing is that enzymes perform this function at body temperature ($\sim 37^\circ\text{C}$) and physiological pH (pH ~ 7), rather than at the conditions that are typically necessary to increase reaction rates (high temperature or pressure, the use of strong oxidizing or reducing agents or strong acids or bases, or a combination of any of these). In addition, enzymes are highly specific in their action; that is, each enzyme catalyzes only one type of reaction in only one compound or a group of structurally related compounds. The compound or compounds on which an enzyme acts are known as its substrates.

Hundreds of enzymes have been purified and studied in an effort to understand how they work so effectively and with such specificity. The resulting knowledge has been used to design drugs that inhibit or activate particular enzymes. An example is the intensive research to improve the treatment of or find a cure for acquired immunodeficiency syndrome (AIDS). AIDS is caused by the human immunodeficiency virus (HIV). Researchers are studying the enzymes produced by this virus and are developing drugs intended to block the action of those enzymes without interfering with enzymes produced by the human body. Several of these drugs have now been approved for use by AIDS patients.

Table 7.4.1: Classes of Enzymes

Class	Type of Reaction Catalyzed	Examples
oxidoreductases	oxidation-reduction reactions	Dehydrogenases catalyze oxidation-reduction reactions involving hydrogen and reductases catalyze reactions in which a substrate is reduced.
transferases	transfer reactions of groups, such as methyl, amino, and acetyl	Transaminases catalyze the transfer of amino group, and kinases catalyze the transfer of a phosphate group.
hydrolases	hydrolysis reactions	Lipases catalyze the hydrolysis of lipids, and proteases catalyze the hydrolysis of proteins
lyases	reactions in which groups are removed without hydrolysis or addition of groups to a double bond	Decarboxylases catalyze the removal of carboxyl groups.
isomerases	reactions in which a compound is converted to its isomer	Isomerases may catalyze the conversion of an aldose to a ketose, and mutases catalyze reactions in which a functional group is transferred from one atom in a substrate to another.
ligases	reactions in which new bonds are formed between carbon and another atom; energy is required	Synthetases catalyze reactions in which two smaller molecules are linked to form a larger one.

The first enzymes to be discovered were named according to their source or method of discovery. The enzyme *pepsin*, which aids in the hydrolysis of proteins, is found in the digestive juices of the stomach (Greek *pepsis*, meaning “digestion”). *Papain*, another enzyme that hydrolyzes protein (in fact, it is used in meat tenderizers), is isolated from papayas. As more enzymes were discovered, chemists recognized the need for a more systematic and chemically informative identification scheme. In the current

numbering and naming scheme, under the oversight of the Nomenclature Commission of the International Union of Biochemistry, enzymes are arranged into six groups according to the general type of reaction they catalyze (Table 7.4.1), with subgroups and secondary subgroups that specify the reaction more precisely.

Figure 7.4.1: Structure of the alcohol dehydrogenase protein (E.C.1.1.1.1) (EE ISOZYME) complexed with nicotinamide adenine dinucleotide (NAD) and zinc (PDB: 1CDO).

Each enzyme is assigned a four-digit number, preceded by the prefix EC—for enzyme classification—that indicates its group, subgroup, and so forth. This is demonstrated in Table 7.4.2 for alcohol dehydrogenase. Each enzyme is also given a name consisting of the root of the name of its substrate or substrates and the *-ase* suffix. Thus urease is the enzyme that catalyzes the hydrolysis of urea.

Table 7.4.2: Assignment of an Enzyme Classification Number

Alcohol Dehydrogenase: EC 1.1.1.1	
The first digit indicates that this enzyme is an oxidoreductase; that is, an enzyme that catalyzes an oxidation-reduction reaction.	
The second digit indicates that this oxidoreductase catalyzes a reaction involving a primary or secondary alcohol.	
The third digit indicates that either the coenzyme NAD ⁺ or NADP ⁺ is required for this reaction.	
The fourth digit indicates that this was the first enzyme isolated, characterized, and named using this system of nomenclature.	
The systematic name for this enzyme is <i>alcohol:NAD⁺ oxidoreductase</i> , while the recommended or common name is alcohol dehydrogenase.	
Reaction catalyzed:	$\text{RCH}_2\text{—OH} + \text{NAD}^+ \rightleftharpoons \text{R—}\overset{\text{O}}{\underset{\text{ }}{\text{C}}}\text{—H} + \text{NADH} + \text{H}^+$

Summary

An enzyme is a biological catalyst, a substance that increases the rate of a chemical reaction without being changed or consumed in the reaction. A systematic process is used to name and classify enzymes.

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CHAPTER OVERVIEW

8: Energy from Food

[8.1: Energy and Its Units](#)

[8.2: Heat Transfer](#)

[8.3: Energy Associated with Phase Changes](#)

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8.1: Energy and Its Units

Learning Objectives

- To define *energy* and *heat*.
- To relate calories to nutrition and exercise.

Energy is the ability to do work. You can understand what this means by thinking about yourself when you feel “energetic.” You feel ready to go—to jump up and get something done. When you have a lot of energy, you can perform a lot of work. By contrast, if you do not feel energetic, you have very little desire to do much of anything. This description is not only applicable to you but also to all physical and chemical processes. The quantity of work that can be done is related to the quantity of energy available to do it.

Energy can be transferred from one object to another if the objects have different temperatures. The transfer of energy due to temperature differences is called heat. For example, if you hold an ice cube in your hand, the ice cube slowly melts as energy in the form of heat is transferred from your hand to the ice. As your hand loses energy, it starts to feel cold.

Because of their interrelationships, energy, work, and heat have the same units. The SI unit of energy, work, and heat is the joule (J). A joule is a tiny amount of energy. For example, it takes about 4 J to warm 1 mL of H₂O by 1°C. Many processes occur with energy changes in thousands of joules, so the kilojoule (kJ) is also common. Another unit of energy, used widely in the health professions and everyday life, is the calorie (cal). The calorie was initially defined as the amount of energy needed to warm 1 g of H₂O by 1°C, but in modern times, the calorie is related directly to the joule, as follows:

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

We can use this relationship to convert quantities of energy, work, or heat from one unit to another.

Although the joule is the proper SI unit for energy, we will use the calorie or the kilocalorie in this chapter because they are widely used by health professionals. Note that the kilocalorie is a synonym for the dietary Calorie, always written with an upper case-C. That is 1000 kilocalories = 1 Calorie.

✓ Example 8.1.1

The energy content of a single serving of bread is 70.0 Cal. What is the energy content in calories? In joules?

Solution

This is a simple conversion-factor problem. Using the relationship 1 Cal = 1,000 cal, we can answer the first question with a one-step conversion:

$$70.0 \text{ Cal} \times \frac{1,000 \text{ cal}}{1 \text{ Cal}} = 70,000 \text{ cal}$$

Then we convert calories into joules

$$70,000 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 293,000 \text{ J}$$

and then kilojoules

$$293,000 \text{ J} \times \frac{1 \text{ kJ}}{1,000 \text{ J}} = 293 \text{ kJ}$$

The energy content of bread comes mostly from carbohydrates.

Exercise

The energy content of one cup of honey is 1,030 Cal. What is its energy content in calories and joules?

Answer

1,030,000 (1.03×10^6) cal; 4,309,520 (4.31×10^6) J

The calorie is used in nutrition to express the energy content of foods. However, because a calorie is a rather small quantity, nutritional energies are usually expressed in **kilocalories (kcal)**, also called **Calories (capitalized; Cal)**. For example, a candy bar may provide 120 Cal (nutritional calories) of energy, which is equal to 120,000 cal. Figure 8.1.1 shows an example.

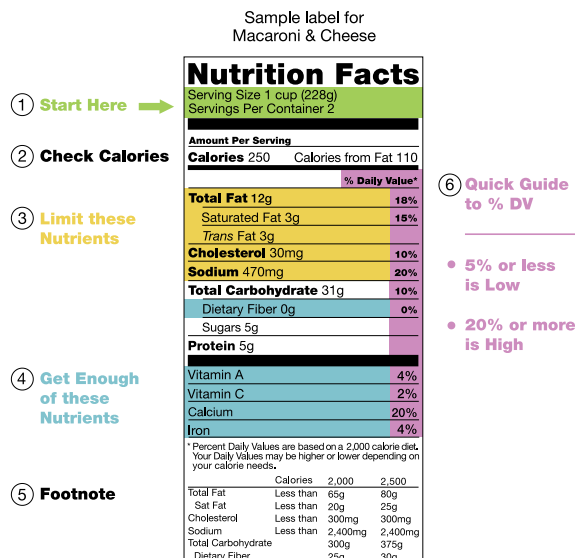


Figure 8.1.1: Figure 8.1.1: Nutritional Energy. A sample nutrition facts label, with instructions from the U.S. Food and Drug Administration. from Wikipedia.

The caloric content of foods is determined by analyzing the food for protein, carbohydrate, fat, water, and “minerals” and then calculating the caloric content using the average values for each component that produces energy (**9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals**). An example of this approach is shown in Table 8.1.1 for a slice of roast beef.

Table 8.1.1: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

Composition	Calories
97.5 g of water	× 0 Cal/g = 0
58.7 g of protein	× 4 Cal/g = 235
69.3 g of fat	× 9 Cal/g = 624
0 g of carbohydrates	× 4 Cal/g = 0
1.5 g of minerals	× 0 Cal/g = 0
Total mass: 227.0 g	Total calories: about 900 Cal

The compositions and caloric contents of some common foods are given in 8.1.2.

Table 8.1.2: Approximate Compositions and Fuel Values of Some Common Foods

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
	Water	Carbohydrate	Protein	Fat		
beer (12 oz)	92	3.6	0.3	0	0.4	150

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
coffee (6 oz)	100	~0	~0	~0	~0	~0
milk (1 cup)	88	4.5	3.3	3.3	0.6	150
egg (1 large)	75	2	12	12	1.6	80
butter (1 tbsp)	16	~0	~0	79	7.1	100
apple (8 oz)	84	15	~0	0.5	0.6	125
bread, white (2 slices)	37	48	8	4	2.6	130
brownie (40 g)	10	55	5	30	4.8	190
hamburger (4 oz)	54	0	24	21	2.9	326
fried chicken (1 drumstick)	53	8.3	22	15	2.7	195
carrots (1 cup)	87	10	1.3	~0	0.4	70

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope. A moderately active individual requires about 2500–3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

To Your Health: Energy Expenditures

Most health professionals agree that exercise is a valuable component of a healthy lifestyle. Exercise not only strengthens the body and develops muscle tone but also expends energy. After obtaining energy from the foods we eat, we need to expend that energy somehow, or our bodies will store it in unhealthy ways (e.g., fat). Like the energy content in food, the energy expenditures of exercise are also reported in kilocalories, usually kilocalories per hour of exercise. These expenditures vary widely, from about 440 kcal/h for walking at a speed of 4 mph to 1,870 kcal/h for mountain biking at 20 mph. Table 8.1.3 lists the energy expenditure for a variety of exercises.

Table 8.1.3: Energy Expenditure of a 180-Pound Person during Selected Exercises

Exercise	Energy Expended (kcal/h)
aerobics, low-level	325
basketball	940
bike riding, 20 mph	830
golfing, with cart	220
golfing, carrying clubs	425
jogging, 7.5 mph	950
racquetball	740
skiing, downhill	520

Exercise	Energy Expended (kcal/h)
soccer	680
walking upstairs	1,200
yoga	280

Because some forms of exercise use more energy than others, anyone considering a specific exercise regimen should consult with his or her physician first.

Summary

Energy is the ability to do work. Heat is the transfer of energy due to temperature differences. Energy and heat are expressed in units of joules.

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8.2: Heat Transfer

Learning Objectives

- To relate heat transfer to temperature change.
- Memorize temperature equations for Celsius, Fahrenheit and Kelvin conversions.
- Understand how body temperature can vary.

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

Temperature Scales

You will recall from previous reading that 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. There are three scales used for reporting temperatures. Figure 8.2.1 compares the three temperature scales: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

Heat transfer

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

Suppose we consider the transfer of heat from the opposite perspective—namely, what happens to a system that gains or loses heat? Generally, the system’s temperature changes. (We will address a few exceptions later.) The greater the original temperature difference, the greater the transfer of heat, and the greater the ultimate temperature change. The relationship between the amount of heat transferred and the temperature change can be written as

$$\text{heat} \propto \Delta T \quad (8.2.1)$$

where $\propto$ means “is proportional to” and ΔT is the **change in temperature of the system**. Any change in a variable is always defined as “the final value minus the initial value” of the variable, so ΔT is $T_{\text{final}} - T_{\text{initial}}$. In addition, the greater the mass of an object, the more heat is needed to change its temperature. We can include a variable representing mass (m) to the proportionality as follows:

$$\text{heat} \propto m\Delta T \quad (8.2.2)$$

To change this proportionality into an equality, we include a proportionality constant. The proportionality constant is called the specific heat and is commonly symbolized by c :

$$\text{heat} = mc\Delta T \quad (8.2.3)$$

Every substance has a characteristic **specific heat**, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express ΔT . The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°C. Table 8.2.1 lists the specific heats for various materials. (For the specific heats of many foods, refer to TheEngineeringToolbox.com.)

Table 8.2.1: Specific Heats of Selected Substances

Substance	c (cal/g•°C)

Substance	c (cal/g•°C)
aluminum (Al)	0.215
aluminum oxide (Al ₂ O ₃)	0.305
bananas	0.8
butter	0.65
beef, loin	0.66
carrots	0.91
eggs	0.76
ice [H ₂ O(s)]	0.492
flour	0.38
lemons	0.91
milk, whole, cows	0.90
pineapple, fresh	0.88
sodium chloride (NaCl)	0.207
steam [H ₂ O(g)]	0.488
water [H ₂ O(l)]	1.00

The proportionality constant c is sometimes referred to as the specific heat capacity or (incorrectly) the heat capacity.

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

✓ For Example (you will not be asked to complete calculations like these). 8.2.3

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

Solution

We can use Equation 8.2.3 to determine the amount of heat, but first we need to determine ΔT . Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

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

The mass is given as 150.0 g, and Table 8.2.1 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into Equation 8.2.3 and solve for amount of heat:

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

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

Exercise

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

Answer

103.4°C

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



Figure 8.2.2: Pots being heated with a wood-burning fire in South India. The heat from the combustion of the wood is transferred to the metal of the pot, and then to the contents of the pot.

Image credit: By Vasanth Bantakal - Own work, CC BY-SA 4.0, <https://commons.wikimedia.org/w/index.php?curid=87224724>

Summary

- Heat transfer is related to temperature change.
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by 1°C.

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8.3: Energy Associated with Phase Changes

Learning Objectives

- Track the heat associated with a phase change.
- Use the terms endothermic and exothermic to describe the transfer of energy during a phase change.

You recall from prior reading that matter can exist in one of several different states, including a gas, liquid, or solid state and that the amount of energy in molecules of matter determines the **state of matter**. You will also recall that

- If heat is added to a substance, such as in melting, vaporization, and sublimation, the process is **endothermic**. In this instance, heat is increasing the speed of the molecules causing them move faster (examples: solid to liquid; liquid to gas; solid to gas).
- If heat is removed from a substance, such as in freezing and condensation, then the process is **exothermic**. In this instance, heat is decreasing the speed of the molecules causing them move slower (examples: liquid to solid; gas to liquid). These changes **release heat** to the surroundings.
- The amount of heat needed to change a sample from solid to liquid would be the same to reverse from liquid to solid. The only difference is the direction of heat transfer.

Phase Change and Heat Transfer

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{\text{fus}} \quad (8.3.1)$$

You will not be asked to complete calculations of the energies involved in the heats of vaporization or heats of fusion. But the process is very similar to the demonstration calculations that were shown in the previous section.

Table 8.3.1 lists the heats of fusion and vaporization for some common substances. Note that the amount of heat required to melt a solid can vary significantly from substance to substance. Also note that the heat of vaporization is always larger than the heat of fusion, which is sensible considering the amount of energy required to add enough kinetic energy to a liquid to separate its particles from each other to become a gas.

Table 8.3.1: Heats of Fusion and Vaporization for Selected Substances

Substance	ΔH_{fus} (cal/g)	ΔH_{vap} (cal/g)
aluminum (Al)	94.0	2,602
gold (Au)	15.3	409
iron (Fe)	63.2	1,504
water (H ₂ O)	79.9	540
sodium chloride (NaCl)	123.5	691
ethanol (C ₂ H ₅ OH)	45.2	200.3
benzene (C ₆ H ₆)	30.4	94.1

Key Takeaway

- There is an energy change associated with any phase change.

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CHAPTER OVERVIEW

9: Cooking - Chemical Change

9.1: Bread and Yeast - an Introduction to Chemical Reactions

9.2: Chemical Change vs. Physical Change

9.3: The Law of Conservation of Matter

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9.6: Acids and Bases

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9.7: Oxidation and Reduction Reactions

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9.8.1: Enzyme Action

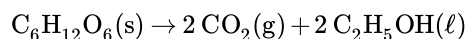
9.8.2: Enzyme Activity

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9.1: Bread and Yeast - an Introduction to Chemical Reactions

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). They convert glucose into carbon dioxide (CO_2) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) in a chemical transformation that is represented as follows:



Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

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9.2: Chemical Change vs. Physical Change

Learning Objectives

- To distinguish between chemical change and physical change.

In a **chemical reaction**, there is a change in the chemical composition of the substances in question. For example, we start with carbon and end up with carbon dioxide, or we start with an egg (with its proteins) and end up with a cooked egg (denatured proteins).

In contrast, in a **physical change** there is a difference in the appearance, smell, or simple display of a sample of matter, but there is no change in the composition of the material. While change is occurring, it is not a chemical change. Thus, we shall simply refer to physical "reactions" as physical changes from now on. For example, ice melts: we start with water (ice, H_2O) and end with water (liquid, H_2O). The composition of the substance did not change. Or consider a piece of paper, torn into bits. We start with paper (one piece) and end with paper (many small pieces).

Introduction

Physical changes are limited to changes that result in a difference in display without changing the composition. Some common changes (but not limited to) are:

- Texture
- Color
- Temperature
- Shape
- Change of State (Boiling Point and Melting Point are significant factors in determining this change.)

Physical properties include many other aspects of a substance. The following are (but not limited to) physical properties.

- Luster
- Malleability
- Ability to be drawn into a thin wire
- Density
- Viscosity
- Solubility
- Mass
- Volume

Any change in these physical properties is referred to as a physical change. For further information, please refer to [Properties of Matter](#).

Chemical changes, on the other hand, are quite different. A chemical change occurs when the substance's composition is changed. When bonds are broken and new ones are formed a chemical change occurs. The following observations suggest chemical changes:

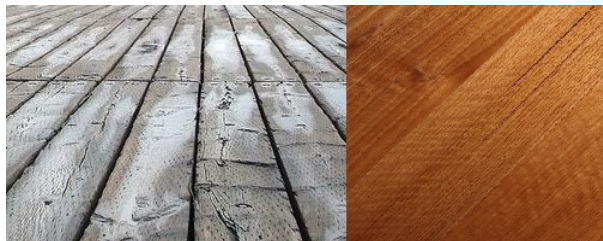
- Change in Temperature
- Change in Color
- Noticeable Odor (after reaction has begun)
- Formation of a Solid in a Solution
- Formation of Bubbles

Note: When two or more reactants are mixed and a change in temperature, color, etc. is noticed, a chemical reaction is probably occurring. These are not definite indicators; a chemical reaction may not be occurring. A change in color is not always a chemical change. If one were to change the color of a substance in a non-chemical reaction scenario, such as painting a car, the change is physical and not chemical. This is because the composition of the car has not changed. Proceed with caution.

Common Physical Changes

Texture

The **texture** of a substance can differ with a physical change. For example, if a piece of wood was sanded, waxed, and polished, it would have a very different texture than it initially had as a rough piece of wood.

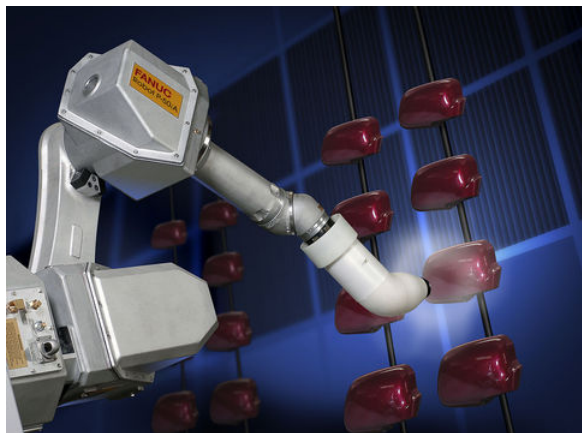


(left) Rough plank boardwalk, Quebec City, Canada (right) Finished mountain ash floor. (CC BY-SA 4.0; [WikiPedant](#) and CC BY-SA 2.5; [MarkAnthonyBoyle](#), respectively).

As you can see, the texture of the finished wood is much smoother than the initial grainy wood.

Color

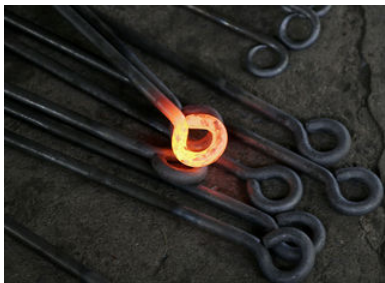
The changing of **color** of a substance is not necessarily an indicator of a chemical change. For example, changing the color of a metal does not change its physical properties. However, in a chemical reaction, a color change is usually an indicator that a reaction is occurring. Painting the metal car does not changing the composition of the metallic substance.



Robotic arm applying paint on car parts. Image use with permission (CC BY-SA 4.0 [RoboGuru](#)).

Temperature

Although we cannot see **temperature** change, unless if a change of state is occurring, it is a physical change.



Hot metalwork. (CC BY-SA-NC 2.0; [flagstaffotos.com.au](#))

One cannot see the pan physically changing shape, color, texture, or any of the other physical properties. However, if one were to touch the pan, it would be incredibly hot and could cause a burn. Sitting idle in a cupboard, this pan would be cold. One cannot assess this change only through visual exposure; the use of a thermometer or other instrument is necessary.

Shape

The **shape** of an object can be changed and the object will still remain true to its chemical composition. For example, if one were to fold money, as shown by the figure below, the money is still chemically the same.

Origami Money



Change of State

The **change of state** is likewise a physical change. In this scenario, one can observe a number of physical properties changing, such as viscosity and shape. As ice turns into water, it does not retain a solid shape and now becomes a viscous fluid. The physical "reaction" for the change of ice into liquid water is:

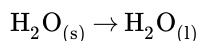


Figure: Ice Melting. used with permission from Wikipedia

The following are the changes of state:

Solid → Liquid	Melting
Liquid → Gas	Vaporization
Liquid → Solid	Freezing
Gas → Liquid	Condensation
Solid → Gas	Sublimation

- If heat is added to a substance, such as in melting, vaporization, and sublimation, the process is **endothermic**. In this instance, heat is increasing the speed of the molecules causing them move faster.
- If heat is removed from a substance, such as in freezing and condensation, then process is **exothermic**. In this instance, heat is decreasing the speed of the molecules causing them move slower.

Physical Properties

Luster

The **luster** of an element is defined as the way it reacts to light. Luster is a quality of a metal. Almost all of the metals, transition metals, and metalloids are lustrous. The non-metals and gases are not lustrous. For example, oxygen and bromine are not lustrous. Shown below is are lustrous paper clips.

Lustrous Paperclips



Malleability

Malleability is also a quality of metals. Metals are said to be malleable. This means that the metals can deform under an amount of stress. For example, if you can hit a metal with a mallet and it deforms, it is malleable. Also, a paperclip can be shaped with bare hands.

Bent Paperclip

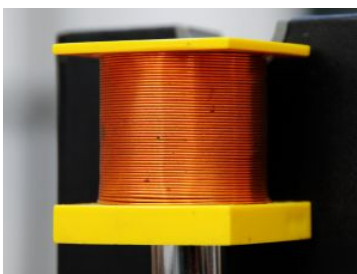


The image shows the malleability of a certain metal as stress is applied to it.

Ability to be drawn into a thin wire

In materials science, this property is called **ductility**. For example, raw copper can be obtained and it can be purified and wrapped into a cord. Once again, this property is characteristic of mainly metals, nonmetals do not possess this quality.

Copper Wire



Density

The **density** of an object is its mass divided by its volume ($d = m/v$). A substance will have a higher density if it has more mass in a fixed amount of volume. For example, take a ball of metal, roughly the size of a baseball, compressed from raw metal. Compare this to a baseball made of paper. The baseball made of metal has a much greater weight to it in the same amount of volume. Therefore the baseball made out of metal has a much higher density. The density of an object will also determine whether it will sink or float in a particular chemical. Water for example has a density of 1 g/cm^3 . Any substance with a density lower than that will float, while any substance with a density above that will sink.



Water and oil in the glass. The lighter density oil (yellow layer) floats on top of the greater density water (clear liquid). (CC BY-SA 4.0; [Victor Blacus](#) via [Wikipedia](#))

Viscosity

Viscosity is defined to be the resistance to deformation of a particular chemical substance when a force is applied to it. In the example below, one can see two cubes falling into two different test tubes. The upper substance shows a violent reaction to the dropping of the cube. The lower substance simply engulfs it slowly without much reaction. The upper substance has a lower viscosity relative to the lower substance, which has very high viscosity. One may even think of viscosity in terms of thickness. The substance with more thickness has higher viscosity than a substance that is deemed "thin." Water has a lower viscosity than honey or magma, which have relatively high viscosities.

Viscosity of Fluids



Viscosity demonstration. The fluid on the left has a lower viscosity than the fluid on the right. (CC SA-BY 4.0; [Synapticrelay](#)).

Common Chemical Changes

The following are all indicators of chemical reactions. For further information on chemical reactions, please refer to [Chemical Reactions](#).

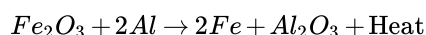
Change in Temperature

A **change in temperature** is characteristic of a chemical change. During an experiment, one could dip a thermometer into a beaker or Erlenmeyer Flask to verify a temperature change. If temperature increases, as it does in most reactions, a chemical change is likely to be occurring. This is different from the physical temperature change. During a physical temperature change, one substance, such as water is being heated. However, in this case, one compound is mixed in with another, and these reactants produce a product. When the reactants are mixed, the temperature change caused by the reaction is an indicator of a chemical change.



Figure: Violent Reaction (Fireworks) with heat as a product

As an example of an exothermic reaction, if Fe_2O_3 is mixed with Al and ignited (often with burning Mg), then the thermite reaction is initiated

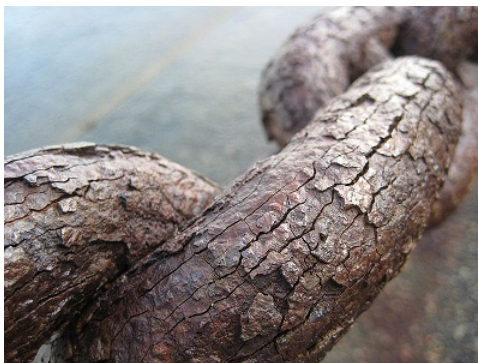


This reaction generates heat as a product and is (very) exothermic.

However, physical changes can be exothermic or endothermic. The melting of an ice cube, which is endothermic, is a change in a physical property and not composition. Thus, it is a physical change.

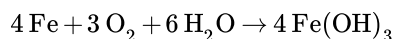
Change in Color

A **change in color** is also another characteristic of a chemical reaction taking place. For example, if one were to observe the rusting of metal over time, one would realize that the metal has changed color and turned orange. This change in color is evidence of a chemical reaction. However, one must be careful; sometimes a change in color is simply the mixing of two colors, but no real change in the composition of the substances in question.



Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt-laden spray, causing surface breakdown, cracking, and flaking of the metal. (CC By-SA 3.0 Unported; [Marlith](#) via [Wikipedia](#))

The reaction above is that of the rusting of iron.



Noticeable Odor

When two or more compounds or elements are mixed and a **scent or odor** is present, a chemical reaction has taken place. For example, when an egg begins to smell, (a rotten egg) a chemical reaction has taken place. This is the result of a chemical decomposition.

Spoiled Egg



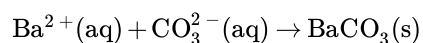
Formation of a Precipitate

The **formation of a precipitate** may be one of the most common signs of a chemical reaction taking place. A precipitate is defined to be a solid that forms inside of a solution or another solid. Precipitates should not be confused with suspensions, which are solutions that are homogeneous fluids with particles floating about in them. For instance, when a soluble carbonate reacts with Barium, a Barium Carbonate precipitate can be observed.

Test Tube



Reaction:



For further information, please refer to [Classification of Matter](#).

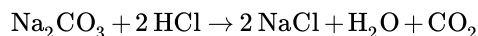
Formation of Bubbles

The **formation of bubbles**, or rather **a gas**, is another indicator of a chemical reaction taking place. When bubbles form, a temperature change could also be taking place. Temperature change and formation of bubbles often occur together. For example, in the following image, one can see a gas spewing. This is the formation of a gas.

Gas Formation



However, most reactions are much more subtle. For instance, if the following reaction occurs, one may notice Carbon Dioxide bubbles forming. If there is enough Hydrochloric Acid, bubbles are visible. If there is not, one can't readily notice the change:



? Exercise 9.2.1

Which of the following is a chemical reaction?

- a. Freezing liquid Mercury
- b. Adding yellow to blue to make green
- c. Cutting a piece of paper into two pieces
- d. Dropping a sliced orange into a vat of Sodium Hydroxide
- e. Filling a balloon with natural air

Answer

D

? Exercise 9.2.2

Which of the following is a physical reaction?

- a. Shattering Glass with a baseball
- b. Corroding Metal
- c. Fireworks Exploding
- d. Lighting a match
- e. Baking a cake

Answer

A

? Exercise 9.2.3

Which of the following is a chemical reaction?

- a. Painting a wall blue
- b. A bicycle rusting
- c. Ice cream melting
- d. Scratching a key across a desk
- e. Making a sand castle

Answer

B

? Exercise 9.2.4

Which of the following is a physical reaction?

- a. Frying an egg
- b. Digesting carrots
- c. A Macbook falling out of a window
- d. Creating ATP in the human body
- e. Dropping a fizzy tablet into a glass of water

Answer

C

? Exercise 9.2.5

Write C for Chemical Reaction or P for Physical Reaction.

- Burning Leaves
- Cutting Diamonds
- Crushing a pencil
- The salivary amylase enzyme that breaks down food in the mouth
- Salt mixing in with water

Answer

- C
- P
- P
- C

e) Neither. This is one of the gray areas of chemical change and physical change. Although the salt has dissociated into Sodium and Chloride ions, it is still salt in water. Salt, initially is actually just a conglomerate of sodium and chloride ions and by dissociating them, just the arrangement of the ions has changed. Please click here for more information

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9.3: The Law of Conservation of Matter

Learning Objectives

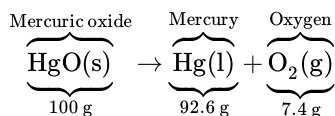
- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*.

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton's Atomic Theory of Matter.

Law of Conservation of Mass

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.



Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

✓ Example 9.3.1

If heating 10 grams of CaCO_3 produces 4.4 g of CO_2 and 5.6 g of CaO , show that these observations are in agreement with the law of conservation of mass.



A sample of calcium carbonate (CaCO_3). (Public Domain; [Walkerma](#)).

Solution

- Mass of the reactants, CaCO_3 : 10 g
- Mass of the products, CO_2 and CaO : $4.4 \text{ g} + 5.6 \text{ g} = 10 \text{ g}$.

Because the mass of the reactants = the mass of the products, the observations are in agreement with the law of conservation of mass.

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the law of conservation of matter, matter is neither created nor destroyed, so we must have the **same number and kind of atoms** after the chemical change as were present before the chemical change.

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Figure 5.1.1 shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

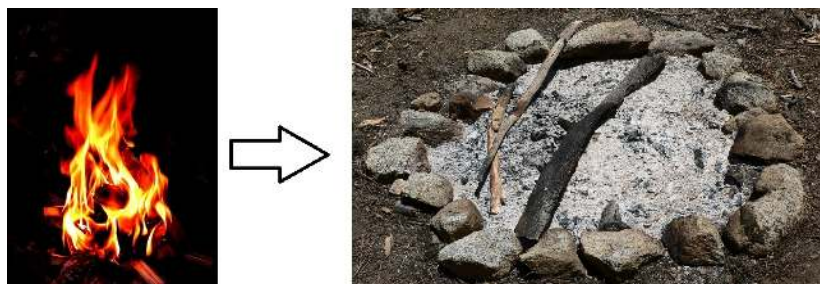


Figure 5.1.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

? Exercise 9.3.1

- What is the law of conservation of matter?
- How does the law of conservation of matter apply to chemistry?

Answer a:

The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

Answer b:

The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

Key Takeaway

The amount of matter in a closed system is conserved.

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9.4: Chemical Equations

Learning Objectives

- Define *chemical reaction*.
- Use a balanced chemical equation to represent a chemical reaction.

Water (H₂O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H₂) and elemental oxygen (O₂) 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 9.4.1 shows a rather dramatic example of this very reaction.

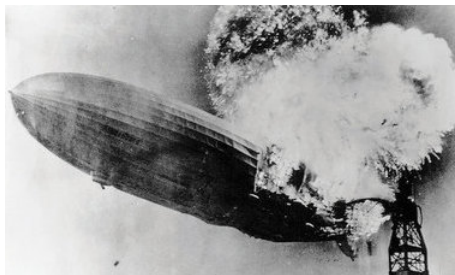


Figure 9.4.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin SS *Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

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** (→) represents the chemical change:



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:



Chemical equations can also be used to describe physical changes. We will see examples of this soon.

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 9.4.2).

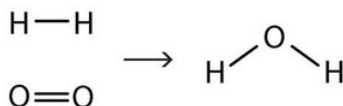


Figure 9.4.2: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

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:



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:



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 **balanced** (Figure 9.4.3). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

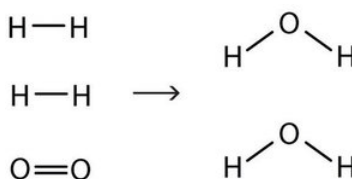


Figure 9.4.3: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

✓ Example 9.4.1

Is each chemical equation balanced?

- $2\text{Na}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Na}_2\text{O}(\text{s})$
- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$
- $\text{AgNO}_3(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$

Solution

- 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.
- 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.
- 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.

? Exercise 9.4.1

Is each chemical equation balanced?

- $2\text{Hg}(\ell) + \text{O}_2(\text{g}) \rightarrow \text{Hg}_2\text{O}_2(\text{s})$
- $\text{C}_2\text{H}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$
- $\text{Mg}(\text{NO}_3)_2(\text{s}) + 2\text{Li}(\text{s}) \rightarrow \text{Mg}(\text{s}) + 2\text{LiNO}_3(\text{s})$

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

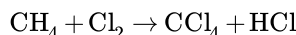
How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a **back-and-forth approach** is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient 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.

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.



Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	Products
1 C atom	1 C atom
4 H ions	1 H ions
2 Cl atom	5 Cl atoms

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:



Reactants	Products
1 C atom	1 C atom
4 H ions	4 H ions
2 Cl atom	8 Cl atoms

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:



Reactants	Products
1 C atom	1 C atom
4 H ions	4 H ions
8 Cl atom	8 Cl atoms

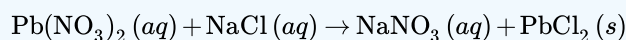
Step 3: Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced. And, the coefficients are in the lowest possible ratio.

✓ Example 9.4.2

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

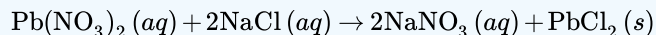
Step 1: Write the skeleton equation with the correct formulas.



Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	1 NO_3^- ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

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 NaNO₃. The result is:



Step 4: The new count for each atom and polyatomic ion becomes:

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	2 NO_3^- ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 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.

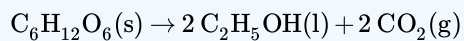
? Exercise 9.4.2

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 ($\text{C}_6\text{H}_{12}\text{O}_6$) are converted to ethanol ($\text{C}_2\text{H}_5\text{OH}$) 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



Key Takeaway

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

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9.5: Some Types of Chemical Reactions

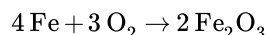
Learning Objectives

- To classify a given chemical reaction into a variety of types.

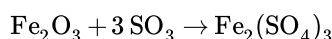
Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

Combination (composition) Reactions

A combination (composition) reaction is a chemical reaction that makes a single substance from two or more reactants. There may be more than one molecule of product in the balanced chemical equation, but there is only one substance produced. For example, the equation



is a combination reaction that produces Fe_2O_3 from its constituent elements — Fe and O_2 . Combination reactions do not have to combine elements, however. The chemical equation



shows a combination reaction in which Fe_2O_3 combines with three molecules of SO_3 to make $\text{Fe}_2(\text{SO}_4)_3$.

✓ Example 9.5.1

Which equations are combination reactions?

- $\text{Co(s)} + \text{Cl}_2(\text{g}) \rightarrow \text{CoCl}_2(\text{s})$
- $\text{CO(g)} + \text{Cl}_2(\text{g}) \rightarrow \text{COCl}_2(\text{g})$
- $\text{N}_2\text{H}_4(\ell) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell)$

Solution

- This is a combination reaction.
- This is a combination reaction. (The compound COCl_2 is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
- This is not a combination reaction.

? Exercise 9.5.1

Which equations are combination reactions?

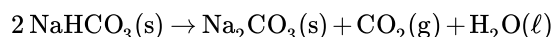
- $\text{P}_4(\text{s}) + 6 \text{Cl}_2(\text{g}) \rightarrow 4 \text{PCl}_3(\text{g})$
- $\text{SO}_3(\ell) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell)$
- $\text{NaOH(s)} + \text{HCl(g)} \rightarrow \text{NaCl(s)} + \text{H}_2\text{O}(\ell)$

Answer

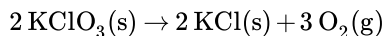
a and b are combination reactions

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction. In a decomposition reaction, a single substance is converted into two or more products. There may be more than one molecule of the reactant, but there is only one substance initially. For example, the equation



is a decomposition reaction that occurs when NaHCO_3 is exposed to heat. Another example is the decomposition of KClO_3 :

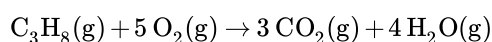


This reaction was once commonly used to generate small amounts of oxygen in the chemistry lab.

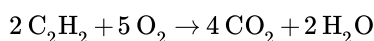
The decomposition reaction of NaHCO_3 is the reaction that occurs when baking soda is poured on a small kitchen fire. The intent is that the H_2O and CO_2 produced by the decomposition will smother the flames.

Combustion Reactions

A combustion reaction occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. An example is propane (C_3H_8), a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.



Another example is the burning of acetylene (C_2H_2) in welding torches:



Oxygen (in its elemental form) is a crucial reactant in combustion reactions.

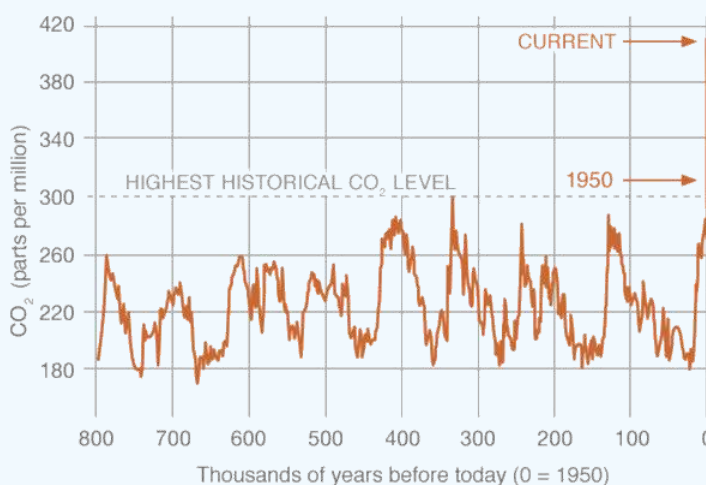
Energy in the form of heat is usually given off as a product in a combustion reaction as well.

✓ Example 9.5.2

Carbon dioxide (CO_2) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. The graph above shows CO_2 levels during the last three glacial cycles, as reconstructed from ice cores.

PROXY (INDIRECT) MEASUREMENTS

Data source: Reconstruction from ice cores.
Credit: NOAA



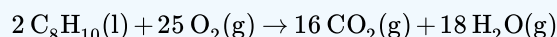
Carbon dioxide is the primary greenhouse gas emitted through human activities. In 2015, CO_2 accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human

activities are altering the carbon cycle—both by adding more CO_2 to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO_2 from the atmosphere. While CO_2 emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2 . An example of how CO_2 can be generated is the **combustion of octane** (C_8H_{10}), a component of gasoline.

Write the balanced equation to represent the combustion of octane.

Solution



The balanced reaction argues that for every two molecules of octane that are burned, 16 molecules of CO_2 are generated.

✓ Example 9.5.2

Identify each type of reaction as either a combination reaction, a decomposition reaction, or a combustion reaction.

- $2 \text{K}(\text{s}) + \text{S}(\text{s}) + 2 \text{O}_2(\text{g}) \rightarrow \text{K}_2\text{SO}_4(\text{s})$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{s}) \rightarrow \text{N}_2(\text{g}) + \text{Cr}_2\text{O}_3(\text{s}) + 4 \text{H}_2\text{O}(\ell)$
- $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell)$

Solution

- Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
- A single substance reacts to make several products, so we have a decomposition reaction.
- Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

? Exercise 9.5.2

Identify each type of reaction as either a combination reaction, a decomposition reaction, or a combustion reaction.

- $\text{C}_2\text{H}_5\text{OH} + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O}$
- $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$
- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Answer a

combustion

Answer b

combination (also combustion)

Answer c

decomposition

Key Takeaway

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

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9.6: Acids and Bases

Acid-base reactions are a common chemical reaction in cooking. Acids and bases can react in a variety of ways, including:

- **Baking**

Baking soda, a base, reacts with acids like vinegar or lemon juice to create carbon dioxide bubbles that make baked goods rise and become fluffy. Baking powder, which contains both baking soda and tartaric acid, also reacts with acids like yogurt or sour cream to create carbon dioxide bubbles.

- **Softening meat**

Acids can help tenderize proteins in meat, such as by marinating meat in lemon juice or tomatoes.

- **Balancing flavors**

Eggs and baking soda can balance out the sour taste of acids and create the ideal consistency in baked goods.

- **Neutralization**

When baking soda and lemon juice react, the citric acid in the lemon juice is neutralized by the sodium bicarbonate in the baking soda, creating salty water and carbon dioxide.

- **Pickling**

The introduction of acid to the pickling process deters the action of microbes that would spoil food, thereby preserving food.

- **Cleaning up after cooking**

Mixing baking soda with an acidic element like vinegar or lemon juice can create a fizzy mixture that can be used to clean kitchen surfaces.

So what are acids and bases and what are the reactions between them? The following sections will address these topics.

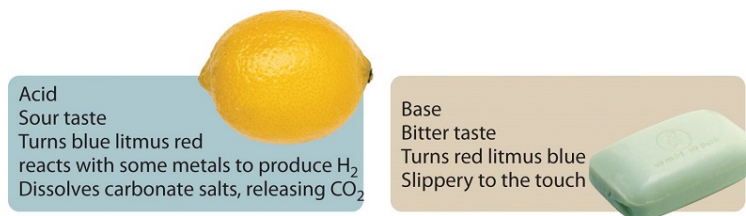
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9.6.1: Acids and Bases - Definition and Neutralization Reactions

Learning Objectives

- To recognize a compound as an Arrhenius acid or an Arrhenius base.
- To describe characteristics of acids and bases.
- To write equations of neutralization reactions.

One way to define a class of compounds is by describing the various characteristics its members have in common. In the case of the compounds known as acids, the common characteristics include a sour taste, the ability to change the color of the vegetable dye *litmus* to red, and the ability to dissolve certain metals and simultaneously produce hydrogen gas. For the compounds called bases, the common characteristics are a slippery texture, a bitter taste, and the ability to change the color of litmus to blue. Acids and bases also react with each other to form compounds generally known as salts.



Although we include their tastes among the common characteristics of acids and bases, we never advocate tasting an unknown chemical!

Chemists prefer, however, to have definitions for acids and bases in chemical terms. The Swedish chemist Svante Arrhenius developed the first chemical definitions of acids and bases in the late 1800s.

Arrhenius defined an acid as **a compound that increases the concentration of hydrogen ion (H^+) in aqueous solution**. Many acids are simple compounds that release a hydrogen cation into solution when they dissolve.

Similarly, Arrhenius defined a base as **a compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution**. Many bases are ionic compounds that have the hydroxide ion as their anion, which is released when the base dissolves in water.

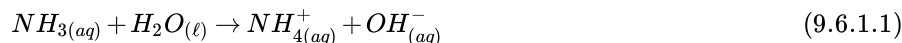
Table 9.6.1.1: Formulas and Names for Some Acids and Bases. The (aq) indicates that these solutions are aqueous, that is, dissolved in water.

Acids		Bases	
Formula	Name	Formula	Name
HCl(aq)	hydrochloric acid	NaOH(aq)	sodium hydroxide (lye)
H ₂ S(aq)	hydrosulfuric acid	KOH(aq)	potassium hydroxide (potash)
HC ₂ H ₃ O ₂ (aq)	acetic acid (the acid in vinegar)	Mg(OH) ₂ (aq)	magnesium hydroxide (milk of magnesia)
H ₂ S(aq)	hydrosulfuric acid (smell of rotting egg)	Ca(OH) ₂ (aq)	calcium hydroxide
H ₂ SO ₄ (aq)	sulfuric acid (battery acid)	NH ₃ (aq)	ammonia
C ₆ H ₈ O ₇ (aq)	citric acid (in citrus fruits)	NaHCO ₃ (aq)	sodium bicarbonate (baking soda)
H ₃ PO ₄ (aq)	phosphoric acid (in many soft drinks)	CaCO ₃ (aq)	calcium carbonate (in Tums)
H ₂ CO ₃ (aq)	carbonic acid	CH ₃ NH ₂ (g)	methylamine (odor of rotten fish)

There are systematic naming rules for acids and bases, but the naming system is beyond the scope of this course.

The name oxygen comes from the Latin meaning “acid producer” because its discoverer, Antoine Lavoisier, thought it was the essential element in acids. Lavoisier was wrong, but it is too late to change the name now.

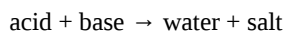
Notice that two bases listed in Table 9.6.1.1—ammonia and methylamine—do not have hydroxide OH as part of its formula. How does this compound increase the amount of hydroxide ion in aqueous solution? Instead of dissociating into hydroxide ions, ammonia molecules react with water molecules by taking a hydrogen ion from the water molecule to produce an ammonium ion and a hydroxide ion:



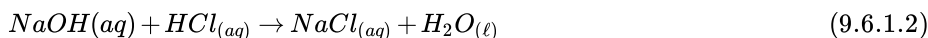
Because this reaction of ammonia with water causes an increase in the concentration of hydroxide ions in solution, ammonia satisfies the Arrhenius definition of a base. Many other nitrogen-containing compounds are bases because they too react with water to produce hydroxide ions in aqueous solution.

Neutralization

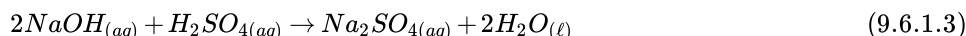
As we noted previously, acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen ion containing compound and the base is a hydroxide ion containing compound, water is also a product. The general reaction is as follows:



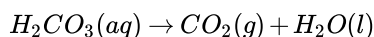
The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:



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



There are a number of examples of acid-base chemistry in everyday life. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.



✓ Example 9.6.1.2

Nitric acid [$HNO_3(aq)$] can be neutralized by calcium hydroxide [$Ca(OH)_2(aq)$]. Write a balanced chemical equation for the reaction between these two compounds and identify the salt it produces.

Solution

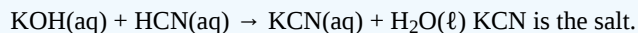
Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of HNO_3 to provide H^+ ions. The balanced chemical equation is as follows: $Ca(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(\ell)$

The salt formed is calcium nitrate.

? Exercise 9.6.1.2

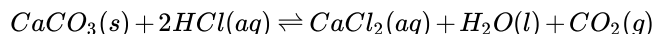
Hydrocyanic acid [HCN(aq)] can be neutralized by potassium hydroxide [KOH(aq)]. Write a balanced chemical equation for the reaction between these two compounds and identify the salt it produces.

Answer



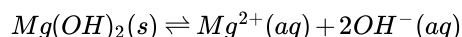
Stomach Antacids

Our stomachs contain a solution of roughly 0.03 M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, CaCO_3 . The reaction,

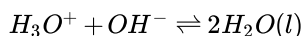


not only neutralizes stomach acid, it also produces $\text{CO}_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, Mg(OH)_2 . It works according to the reaction:



The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :



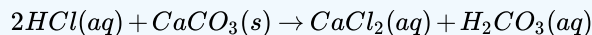
This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, Al(OH)_3 , as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

✓ Example 9.6.1.3

Assume that the stomach of someone suffering from acid indigestion contains hydrochloric acid HCl. Write the balanced reaction for the reaction of HCl with the base in Tums, CaCO_3 .

Solution

The balanced chemical equation for the reaction is:



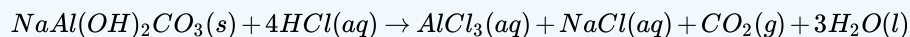
Each carbonate ion can react with 2 mol of H^+ to produce H_2CO_3 , which rapidly decomposes to H_2O and CO_2 .

ise

Assume that as a result of overeating, a person's stomach contains too much HCl. The person consumes Roloids tablets that contain the base $\text{NaAl(OH)}_2\text{CO}_3$. The neutralization reaction can be written as follows. Can you balance the reaction?



Answer



Key Takeaway

- An Arrhenius acid increases the H^+ ion concentration in water, while an Arrhenius base increases the OH^- ion concentration in water.

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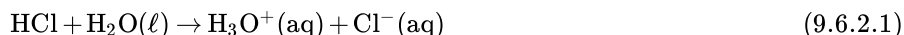
9.6.2: Water - Both an Acid and a Base

Learning Objectives

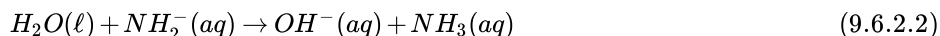
- Examine equations to identify water acting as an acid or as a base.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. Consider the example of dissolving of HCl in H_2O :



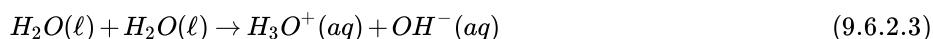
In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:



In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:



This process is called the **autoionization of water** (Figure 9.6.2.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

Note

It is rare to have truly pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

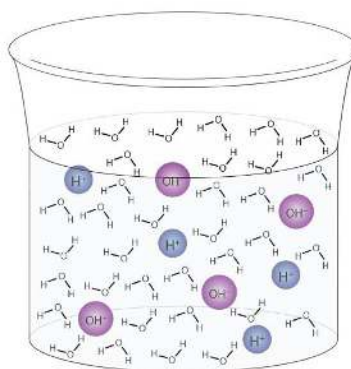


Figure 9.6.2.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

✓ Example 9.6.2.1

Identify water behaving as either a Brønsted-Lowry acid or a Brønsted-Lowry base in the examples below.

1. $\text{H}_2\text{O}(\ell) + \text{NO}_2^-(\text{aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq})$
2. $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $\text{OH}^-(\text{aq})$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $\text{HC}_2\text{H}_3\text{O}_2$, becoming $\text{H}_3\text{O}^+(\text{aq})$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

? Exercise 9.6.2.2

Identify water behaving as either a Brønsted-Lowry acid or a Brønsted-Lowry base in the examples below.

1. $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$
2. $\text{H}_2\text{O}(\ell) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{OH}^-(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

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9.6.3: The Strengths of Acids and Bases, and the pH Scale

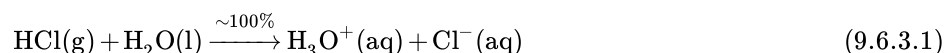
Learning Objectives

- Describe the difference between strong and weak acids and bases.
- Use K_a values to rank weak acids in order of higher or lower acidity.
- Use the pH scale to describe acids and bases and rank solutions for being acidic, basic, and neutral.

Acids and bases do not all demonstrate the same degree of chemical activity in solution. Different acids and bases have different strengths.

Strong and Weak Acids

Let us consider the strengths of acids first. A small number of acids ionize completely in aqueous solution. For example, when HCl dissolves in water, every molecule of HCl separates into a hydronium ion and a chloride ion:



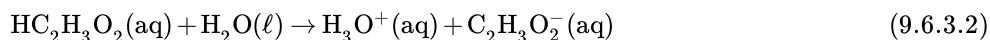
HCl(aq) is one example of a **strong acid**, which is a compound that is essentially **100% ionized** in aqueous solution. There are very few strong acids. The important ones are listed in Table 9.6.3.1.

Table 9.6.3.1: Strong Acids and Bases (All in Aqueous Solution)

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO ₃	Mg(OH) ₂
H ₂ SO ₄	Ca(OH) ₂
HClO ₄	

By analogy, a strong base is a compound that is essentially 100% ionized in aqueous solution. As with acids, there are only a few strong bases, which are also listed in Table 9.6.3.1.

If an acid is **not listed** in Table 9.6.3.1, it is likely a **weak acid**, which is a compound that is not 100% ionized in aqueous solution. Similarly, a weak base is a compound that is not 100% ionized in aqueous solution. For example, acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) is a weak acid. The ionization reaction for acetic acid is as follows:

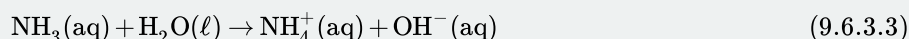


Depending on the concentration of $\text{HC}_2\text{H}_3\text{O}_2$, the ionization reaction may occur only for 1%–5% of the acetic acid molecules.

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 [$\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$]. In a medicine chest, one may find a bottle of **vitamin C** tablets; the chemical name of vitamin C is ascorbic acid ($\text{HC}_6\text{H}_7\text{O}_6$).

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:



Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



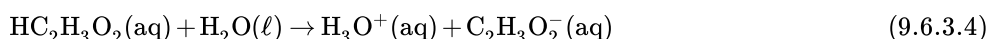
Figure 9.6.3.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

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.

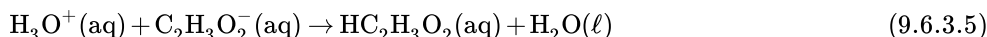
Another important safety tip for using household cleaners is to never use bleach with other cleaning products. The cleaning products can react with bleach to produce chlorine gas and chloramines which are toxic and deadly.

Chemical Equilibrium in Weak Acids and Bases

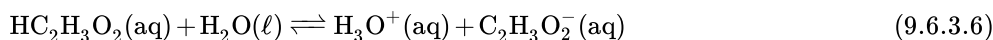
The behavior of **weak acids and bases** illustrates a key concept in chemistry. Does the chemical reaction describing the ionization of a weak acid or base just stop when the acid or base is done ionizing? Actually, no. Rather, the reverse process—the reformation of the molecular form of the acid or base—occurs, ultimately at the same rate as the ionization process. For example, the ionization of the weak acid $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$ is as follows:



The reverse process also begins to occur:



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:



The $\rightleftharpoons$ implies that **both the forward and reverse reactions** are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

✓ Example 9.6.3.1: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

- $\text{HNO}_2(\text{aq})$
- $\text{C}_5\text{H}_5\text{N}(\text{aq})$

Solution

- $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq})$

? Exercise 9.6.3.1

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

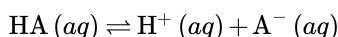
- $HF_{(aq)}$
- $AgOH_{(aq)}$
- $CH_3NH_2(aq)$

Answer

- $HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$
- $AgOH(aq) \rightleftharpoons Ag^+(aq) + OH^-(aq)$
- $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

Acid Ionization Constant, K_a

Chemists have created a rating system that measures the strength of a weak acid. It is based on the ionization reaction for a general weak acid, HA:



The numerical value of K_a is a reflection of the strength of the acid. Several examples are shown in the table below. Weak acids with larger K_a values are stronger than acids with smaller K_a values.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table 9.6.3.2: Acid Ionization Constants at 25°C

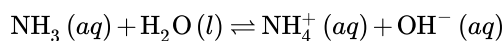
Name of Acid	K_a Value*
Oxalic acid (found in spinach and rhubarb)	5.6×10^{-2}
Citric acid (in citrus foods)	7.1×10^{-4}
Lactic acid (in dairy foods and fermented foods)	1.4×10^{-4}
Malic acid (found in apples and other fruits and vegetables)	4.0×10^{-4}
Acetic acid (found in vinegar and fermented foods)	1.8×10^{-5}
Carbonic acid (dissolved in water to make carbonated drinks)	4.2×10^{-7}

*Some acids, such as citric acid, malic acid, and carbonic acid, have more than one acidic proton and are polyprotic. In this table, the K_a value for only the most acidic H^+ is listed.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.



As with acids, chemists rate the strength of bases based, and use a numerical value of K_b . Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. Table 9.6.3.3 is a listing of base ionization constants for several weak bases.

Table 9.6.3.3: Base Ionization Constants at 25°C

Name of Base	K_b
Methylamine	5.6×10^{-4}
Ammonia	1.8×10^{-5}
Pyridine	1.7×10^{-9}
Acetate ion	5.6×10^{-10}
Fluoride ion	1.4×10^{-11}
Urea	1.5×10^{-14}

The Ion-Product of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

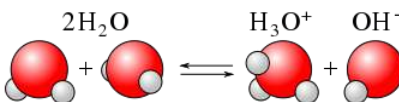
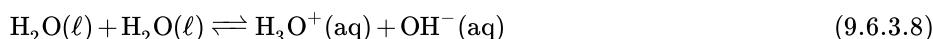
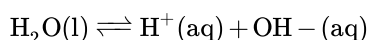


Figure 9.6.3.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:



We often use the simplified form of the reaction:



The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w .

$$K_w = [H^+][OH^-] \\ = 1.0 \times 10^{-14}$$

This means that...

- For solutions that are acidic, the concentration of H^+ or $[H^+]$ is greater than $1.0 \times 10^{-7} M$
- For solutions that are basic, the concentration of OH^- or $[OH^-]$ is greater than $1.0 \times 10^{-7} M$
- For neutral solutions, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} M$

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure 9.6.3.3 illustrates this relationship, along with some examples of various solutions.

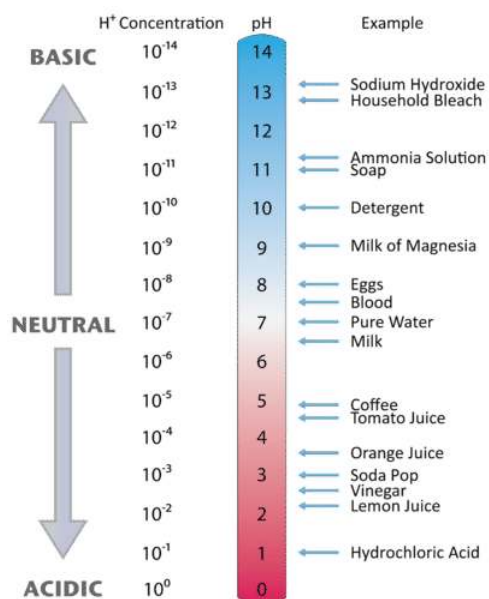


Figure 9.6.3.3: The relationship between $[H^+]$ and pH values for several common materials.

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 9.6.3.4.

Table 9.6.3.4 Acidic, Basic and Neutral pH Values

Acidic, Basic and Neutral pH Values		
Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	$pH < 7$
neutral	$[H^+] = [OH^-]$	$pH = 7$
basic	$[H^+] < [OH^-]$	$pH > 7$

✓ Example 9.6.3.3

For each of the following solutions, classify them as acidic, basic, or neutral:

- pickle juice, pH 3.3
- apricot juice, pH 4.0
- drinking water, pH 7.2

Solution

The pH scale ranks items from most acidic (low pH) to most basic (high pH), with $pH = 7$ for a neutral solution.

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

- acidic (pH is less than 7)
- acidic (pH is less than 7)
- basic (pH is more than 7)

Exercise

Consider the following solutions:

Olive brine, pH 3.7

Shrimp puree, pH 7.0

Hominy cooking water, pH 7.5

Grapefruit juice, pH 3.1

- Which is the most acidic?
- Which is the most basic?
- Which is neutral?

Answer

- Grapefruit juice
- Hominy cooking water
- Shrimp puree

Table 9.6.3.5 lists the pH of several common solutions. The most acidic among the listed solutions is battery acid with the lowest pH value (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.

Table 9.6.3.5: The pH Values of Some Common Solutions

Solution	pH
battery acid	0.3
stomach acid	1–2
lemon or lime juice	2.1
vinegar	2.8–3.0
Coca-Cola	3
wine	2.8–3.8
beer	4–5
coffee	5
milk	6
urine	6
pure H ₂ O	7
(human) blood	7.3–7.5
sea water	8
antacid (milk of magnesia)	10.5
NH ₃ (1 M)	11.6
bleach	12.6
NaOH (1 M)	14.0

✓ Example 9.6.3.4

Label each solution as acidic, basic, or neutral based only on the stated *pH*.

- milk of magnesia, pH = 10.5
- pure water, pH = 7
- wine, pH = 3.0

Solution

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

Exercise

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

- human blood with $pH = 7.4$
- household ammonia with $pH = 11.0$
- cherries with $pH = 3.6$

Answer

- slightly basic
- basic
- acidic

Key Takeaways

- Acids and bases can be strong or weak depending on the extent of ionization in solution.
- Most chemical reactions reach equilibrium at which point there is no net change.
- The ion-product of $[\text{H}^+][\text{OH}^-]$ in an aqueous solution remains constant.
- A **pH** value is simply the *negative* of the logarithm of the H^+ ion concentration ($-\log[\text{H}^+]$).
- The pH scale is used to succinctly communicate the acidity or basicity of a solution.
- A solution is **acidic** if $pH < 7$.
- A solution is **basic** if $pH > 7$.
- A solution is **neutral** if $pH = 7$.

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9.7: Oxidation and Reduction Reactions

In the previous sections you learned about acids and bases, the pH scale, and acid-base reactions. In the following sections you will learn about another kind of reaction that appears in the chemistry of cooking: oxidation and reduction reactions. Chemists have a nickname for these kinds of reactions, "redox reactions." Here are a few different places where we see redox reactions playing a role.

- **Oxidation**

When food is exposed to oxygen it can causing it to lose or change flavor, color, texture, and nutritional value.

- **Carmelization.** Those delightful caramel and toasty flavors that come from the browning of sugars and starches arise from oxidation of the sugars and starches. Other browning arises from a collection of protein oxidations - leading to the roasted meat flavors arising from a process called the Maillard reaction.
- **Rancidity.** Oxygen can react with the double bonds present in fatty acids, which produces shorter-chain fatty acids. These shorter-chain fatty acids can produce odors and flavors which we detect as rancidity.
- **Browning.** Oxidation is also observed in fruits and vegetables, causing them to turn brown, a process called enzymic browning. For example, if you cut an apple or avocado and leave it out for more than an hour, the tissue will be exposed to oxygen and the enzyme polyphenol oxidase will trigger, causing the fruit to turn brown.

- **Reduction**

- **Anaerobic fermentation.** Anaerobic means "without air" - can be used to prepare pickles, cheeses, cured meats, coffee and tea, and more. While some fermentation is aerobic, the anaerobic fermentation phases lead to a wide range of flavor profiles that arise from acetaldehyde, lactic acid, acetic acid, and other acids.

- **Antioxidants**

Molecules that can prevent oxidation reactions from occurring and food from spoiling too quickly. Antioxidant molecules are reducing agents, which means they cause other substances to be reduced while being oxidized themselves. Many brightly colored fruits and berries are rich in polyphenols, which are complex antioxidant compounds. Vitamin E and vitamin C are also antioxidants that can help prevent oxidation. Vitamin E prevents fats from becoming rancid, while vitamin C can be found in citrus fruits like oranges, lemons, and limes.

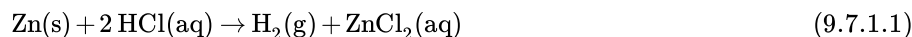
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9.7.1: Oxidation-Reduction (Redox) Reactions

Learning Objectives

- To identify a chemical reaction as an oxidation-reduction reaction.

Before jumping into redox reactions with food molecules, let us first look at some simple cases. For example, when zinc metal is submerged into a quantity of aqueous HCl, the following reaction occurs (Figure 9.7.1.1):

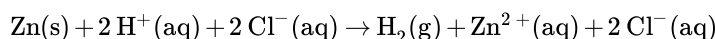


This is one example of what is sometimes called a *single replacement reaction* because Zn replaces H in combination with Cl.



Figure 9.7.1.1: 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 9.7.1.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:



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.

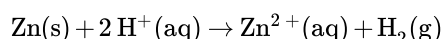
To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called **oxidation**.

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.

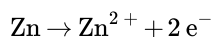
As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species 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,

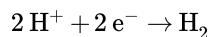


zinc atoms are oxidized to Zn^{2+} . The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:



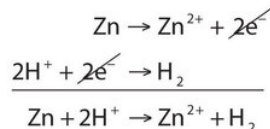
This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a $2+$ ion. With half reactions, there is one more item to balance: the overall charge on each side of 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:



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.

To verify that the overall reaction is simply the combination of the two half reactions, confirm that the two half-reactions can be added together to give the original reaction:



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.)

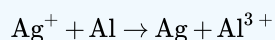
Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel.** The following example demonstrates this process.

✓ Example 9.7.1.1: 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.

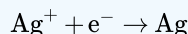
Solution

We start by using symbols of the elements and ions to represent the reaction:



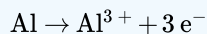
The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of $+1$ on the left but a charge of $+3$ on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag :

Reduction half-reaction:

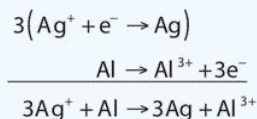


Aluminum is oxidized, losing three electrons to change from Al to Al^{3+} :

Oxidation half-reaction:



To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:



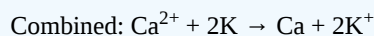
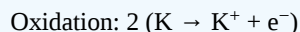
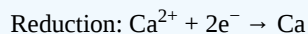
Now the equation is balanced, not only in terms of elements but also in terms of charge.

- The **substance oxidized** is the reactant that had undergone oxidation: Al
- The **substance reduced** is the reactant that had undergone reduction: Ag^+

? Exercise 9.7.1.1

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 and the substance reduced.

Answer



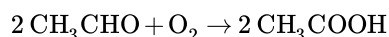
- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: Ca^{2+}

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

Observing Oxidation and Reduction in Larger Molecules

While tracking electrons is the gold standard definition when it comes to identifying oxidation and reduction processes, there are other indicators that can be helpful, especially when looking at larger molecules.

Follow the Oxygen: The original meaning of **oxidation** was “adding oxygen,” so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule **loses oxygen** atoms, the molecule is being reduced. For example, the acetaldehyde (CH_3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).



Thus, acetaldehyde is being oxidized.

Follow the Hydrogen: 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 ($\text{CH}_3\text{CH}_2\text{OH}$), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

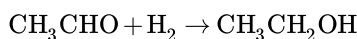


Table shows how each process affects the change in oxygen and change in hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

✓ Example 9.7.1.2

In each conversion, indicate whether oxidation or reduction is occurring, and describe the indicator used to reach that conclusion.

- $\text{N}_2 \rightarrow \text{NH}_3$
- $\text{CH}_3\text{CH}_2\text{OHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3$
- $\text{HCHO} \rightarrow \text{HCOOH}$

Solution

- Hydrogen is being added to the original reactant molecule, so reduction is occurring.
- Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
- Oxygen is being added to the original reactant molecule, so oxidation is occurring.

? Exercise 9.7.1.2

In each conversion, indicate whether oxidation or reduction is occurring, and describe the indicator used to reach that conclusion.

- a. $\text{CH}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- b. $\text{NO}_2 \rightarrow \text{N}_2$
- c. $\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_3$

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

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9.7.2: Redox Reactions in Organic Chemistry and Biochemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in cooking, of course, but also in the production of the foods that we eat, all of which come from photosynthesis (plant foods) and respiration (animal-based foods).



Figure 9.7.2.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. from Wikipedia.

As a reminder: redox processes can be identified by tracking the exchange of electrons, or by following the amount of oxygen or hydrogen bonded to the species in the reaction. To review these tracking methods, return to the prior section.

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 9.7.2.1).

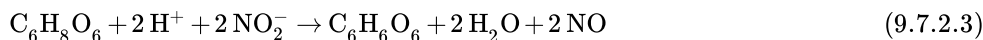


In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of **glucose** ($\text{C}_6\text{H}_{12}\text{O}_6$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:



In this reaction, the glucose molecule is oxidized because it gained oxygen atoms from a 1:1 ratio of carbon to oxygen to a 1:2 ratio of carbon to oxygen in CO_2 . The oxygen in the reaction is reduced - it gains hydrogen to form water, and carbon to form carbon dioxide.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (**vitamin C**; $\text{C}_6\text{H}_8\text{O}_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):



If reaction in Equation 9.7.2.3 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.

Tocopherol (**vitamin E**) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure 9.7.2.2).



Figure 9.7.2.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 9.7.2.3). The overall change that occurs is as follows:



In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure 9.7.2.3: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

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9.8: Reactions in Proteins

A char-grilled steak, a seared slice of tofu, the toasted edges of cheese on a lasagna. These mouth-watering flavors and textures arise from the Maillard reaction, a complex series of reactions that involve cooked protein.

Banana peels brown over time, pineapple prevents a gelatin dessert from setting up, meat tenderizer powder does its work. These examples show another side of proteins - enzymes at work.

In this section, you will be looking closely at proteins. [Prior readings](#) introduced you to amino acids, proteins, and enzymes. Please review these if you need some background before studying the role of enzymes in reactions.



Images: Wikipedia.

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9.8.1: Enzyme Action

Learning Objectives

- To describe the interaction between an enzyme and its substrate.

If you would like to review amino acids, proteins, and the definition of an enzyme, please revisit [Chapter 7](#).

Enzyme-catalyzed reactions occur in at least two steps. In the first step, an enzyme molecule (E) and the substrate molecule or molecules (S) collide and react to form an intermediate compound called the *enzyme-substrate* (E-S) *complex*. (This step is reversible because the complex can break apart into the original substrate or substrates and the free enzyme.) Once the E-S complex forms, the enzyme is able to catalyze the formation of product (P), which is then released from the enzyme surface:



Hydrogen bonding and other interactions hold the enzyme and substrate together in the complex. The structural features or functional groups on the enzyme that participate in these interactions are located in a cleft or pocket on the enzyme surface. This pocket, where the enzyme combines with the substrate and transforms the substrate to product is called the **active site of the enzyme** (Figure 9.8.1.1).

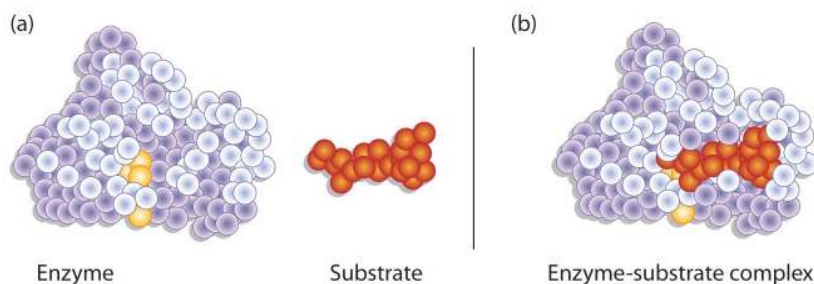


Figure 9.8.1.1: Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: NADP⁺ (a) unbound and (b) bound. The NADP⁺ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.

The active site of an enzyme possesses a unique conformation (including correctly positioned bonding groups) that is complementary to the structure of the substrate, so that the enzyme and substrate molecules fit together in much the same manner as a key fits into a tumbler lock. In fact, an early model describing the formation of the enzyme-substrate complex was called the lock-and-key model (Figure 9.8.1.2). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

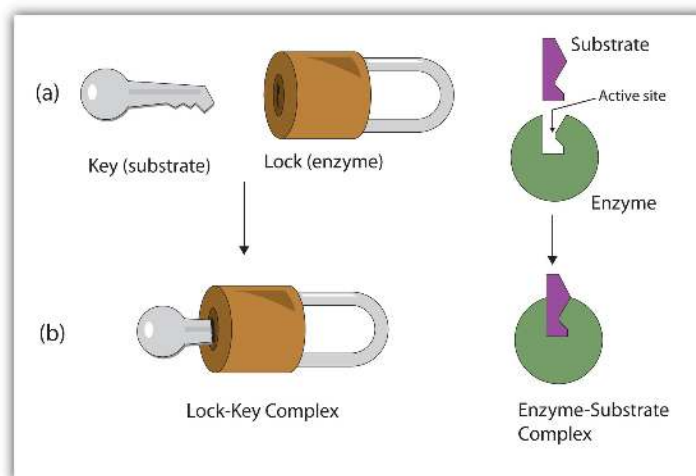


Figure 9.8.1.2: The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.

Working out the precise three-dimensional structures of numerous enzymes has enabled chemists to refine the original lock-and-key model of enzyme actions. They discovered that the binding of a substrate often leads to a large conformational change in the enzyme, as well as to changes in the structure of the substrate or substrates. The current theory, known as the induced-fit model, says that enzymes can undergo a change in conformation when they bind substrate molecules, and the active site has a shape complementary to that of the substrate only *after* the substrate is bound, as shown for hexokinase in Figure 9.8.1.3 After catalysis, the enzyme resumes its original structure.

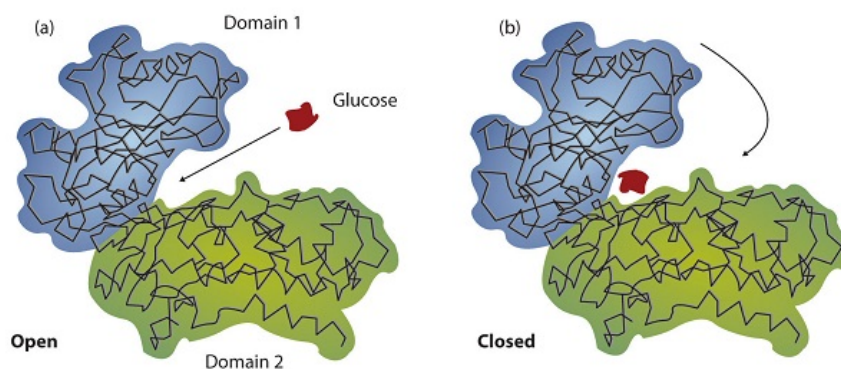


Figure 9.8.1.3: The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.

The structural changes that occur when an enzyme and a substrate join together bring specific parts of a substrate into alignment with specific parts of the enzyme's active site. Amino acid side chains in or near the binding site can then act as acid or base catalysts, provide binding sites for the transfer of functional groups from one substrate to another or aid in the rearrangement of a substrate. The participating amino acids, which are usually widely separated in the primary sequence of the protein, are brought close together in the active site as a result of the folding and bending of the polypeptide chain or chains when the protein acquires its tertiary and quaternary structure. Binding to enzymes brings reactants close to each other and aligns them properly, which has the same effect as increasing the concentration of the reacting compounds.

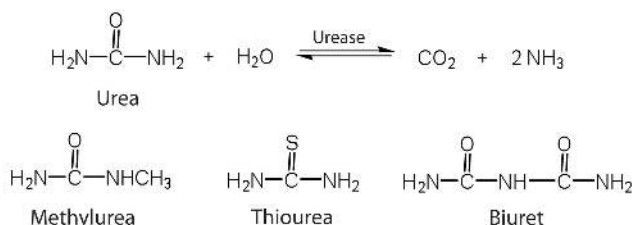
✓ Example 9.8.1.1

- What type of interaction would occur between an OH group present on a substrate molecule and a functional group in the active site of an enzyme?
- Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

Solution

- An OH group would most likely engage in hydrogen bonding with an appropriate functional group present in the active site of an enzyme.
- Several amino acid side chains would be able to engage in hydrogen bonding with an OH group. One example would be asparagine, which has an amide functional group.

One characteristic that distinguishes an enzyme from all other types of catalysts is its *substrate specificity*. Some enzymes act on a single substrate, while other enzymes act on any of a group of related molecules containing a similar functional group or chemical bond. Some enzymes even distinguish between D- and L-stereoisomers, binding one stereoisomer but not the other. Urease, for example, is an enzyme that catalyzes the hydrolysis of a single substrate—urea—but not the closely related compounds methyl urea, thiourea, or biuret. The enzyme carboxypeptidase, on the other hand, is far less specific. It catalyzes the removal of nearly any amino acid from the carboxyl end of any peptide or protein.



Enzyme specificity results from the uniqueness of the active site in each different enzyme because of the identity, charge, and spatial orientation of the functional groups located there. It regulates cell chemistry so that the proper reactions occur in the proper place at the proper time. Clearly, it is crucial to the proper functioning of the living cell.

Summary

A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product. The substrate binds to the enzyme primarily through hydrogen bonding and other electrostatic interactions. The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate. Enzymes exhibit varying degrees of substrate specificity.

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9.8.2: Enzyme Activity

Learning Objectives

- To describe how pH, temperature, and the concentration of an enzyme and its substrate influence enzyme activity.

Recall that the enzyme is the catalyst, and the molecule that the enzyme acts upon is called the substrate.

The single most important property of enzymes is the ability to increase the rates of reactions occurring in living organisms, a property known as *catalytic activity*. Because most enzymes are proteins, their activity is affected by factors that disrupt protein structure, as well as by factors that affect catalysts in general. Factors that disrupt protein structure include temperature and pH; factors that affect catalysts in general include reactant or substrate concentration and catalyst or enzyme concentration. The activity of an enzyme can be measured by monitoring either the rate at which a substrate disappears or the rate at which a product forms.

Concentration of Substrate

In the presence of a given amount of enzyme, the rate of an enzymatic reaction increases as the substrate concentration increases until a limiting rate is reached, after which further increase in the substrate concentration produces no significant change in the reaction rate (part (a) of Figure 9.8.2.1). At this point, so much substrate is present that essentially all of the enzyme active sites have substrate bound to them. In other words, the enzyme molecules are saturated with substrate. The excess substrate molecules cannot react until the substrate already bound to the enzymes has reacted and been released (or been released without reacting).

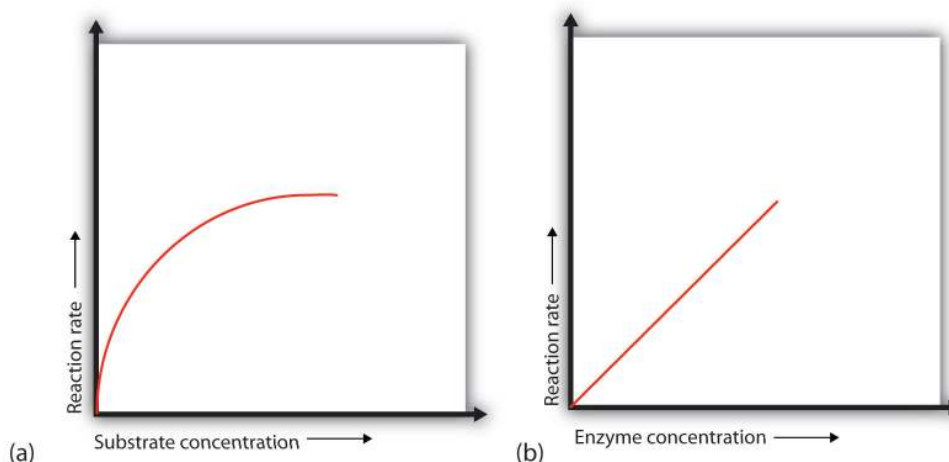


Figure 9.8.2.1: Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.

Let's consider an analogy. Ten taxis (enzyme molecules) are waiting at a taxi stand to take people (substrate) on a 10-minute trip to a concert hall, one passenger at a time. If only 5 people are present at the stand, the rate of their arrival at the concert hall is 5 people in 10 minutes. If the number of people at the stand is increased to 10, the rate increases to 10 arrivals in 10 minutes. With 20 people at the stand, the rate would still be 10 arrivals in 10 minutes. The taxis have been "saturated." If the taxis could carry 2 or 3 passengers each, the same principle would apply. The rate would simply be higher (20 or 30 people in 10 minutes) before it leveled off.

Concentration of Enzyme

When the concentration of the enzyme is significantly lower than the concentration of the substrate (as when the number of taxis is far lower than the number of waiting passengers), the rate of an enzyme-catalyzed reaction is directly dependent on the enzyme concentration (part (b) of Figure 9.8.2.1). This is true for any catalyst; the reaction rate increases as the concentration of the catalyst is increased.

Temperature

A general rule of thumb for most chemical reactions is that a temperature rise of 10°C (18°F) approximately doubles the reaction rate. To some extent, this rule holds for all enzymatic reactions. After a certain point, however, an increase in temperature causes a decrease in the reaction rate, due to denaturation of the protein structure and disruption of the active site (part (a) of Figure 9.8.2.2). For many proteins, denaturation occurs between 45°C and 55°C . Furthermore, even though an enzyme may appear to have a maximum reaction rate between 40°C and 50°C , most biochemical reactions are carried out at lower temperatures because enzymes are not stable at these higher temperatures and will denature after a few minutes.

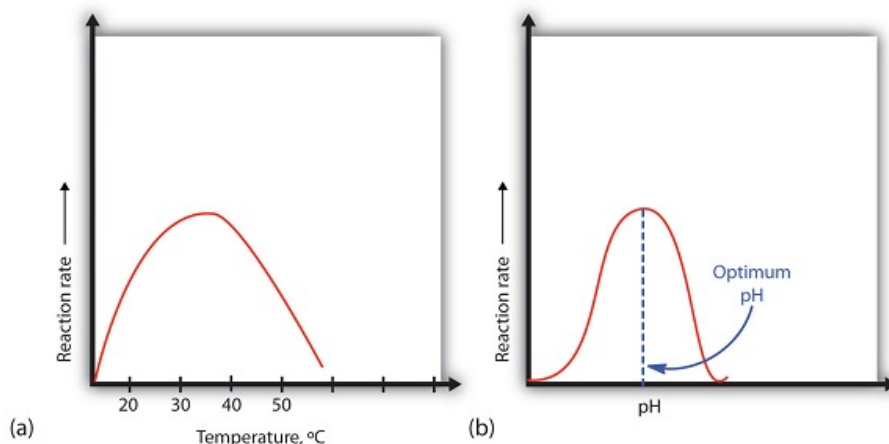


Figure 9.8.2.2: Temperature and pH versus Concentration. (a) This graph depicts the effect of temperature on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph depicts the effect of pH on the rate of a reaction that is catalyzed by a fixed amount of enzyme.

At 0°C and 100°C , the rate of enzyme-catalyzed reactions is nearly zero. This fact has several practical applications. We sterilize objects by placing them in boiling water, which denatures the enzymes of any bacteria that may be in or on them. We preserve our food by refrigerating or freezing it, which slows enzyme activity. When animals go into hibernation in winter, their body temperature drops, decreasing the rates of their metabolic processes to levels that can be maintained by the amount of energy stored in the fat reserves in the animals' tissues.

Hydrogen Ion Concentration (pH)

Because most enzymes are proteins, they are sensitive to changes in the hydrogen ion concentration or pH. Enzymes may be denatured by extreme levels of hydrogen ions (whether high or low); *any* change in pH, even a small one, alters the degree of ionization of an enzyme's acidic and basic side groups and the substrate components as well. Ionizable side groups located in the active site must have a certain charge for the enzyme to bind its substrate. Neutralization of even one of these charges alters an enzyme's catalytic activity.

An enzyme exhibits maximum activity over the narrow pH range in which a molecule exists in its properly charged form. The median value of this pH range is called the optimum pH of the enzyme (part (b) of Figure 9.8.2.2). With the notable exception of gastric juice (the fluids secreted in the stomach), most body fluids have pH values between 6 and 8. Not surprisingly, most enzymes exhibit optimal activity in this pH range. However, a few enzymes have optimum pH values outside this range. For example, the optimum pH for pepsin, an enzyme that is active in the stomach, is 2.0.

Summary

Initially, an increase in substrate concentration leads to an increase in the rate of an enzyme-catalyzed reaction. As the enzyme molecules become saturated with substrate, this increase in reaction rate levels off. The rate of an enzyme-catalyzed reaction increases with an increase in the concentration of an enzyme. At low temperatures, an increase in temperature increases the rate of an enzyme-catalyzed reaction. At higher temperatures, the protein is denatured, and the rate of the reaction dramatically decreases. An enzyme has an optimum pH range in which it exhibits maximum activity.

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